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HEAT AND FREE ENERGY OF FORMATION OF DEUTERIUM OXIDE*

By Frederick D. Rossini, John W. Knowlton, and Herrick L. Johnston[1]

ABSTRACT

Calorimetric measurements of the ratio of the heat evolved in the formation of 1 mole of liquid deuterium oxide, from gaseous deuterium and ordinary oxygen, to the heat evolved in the formation of 1 mole of ordinary liquid water, from gaseous ordinary hydrogen and oxygen, yielded the value 1.030 68 ±0.000 29 for 25° C and a constant pressure of 1 atmosphere.

Calorimetric measurements of the ratio of the heat of vaporization of 1 mole of deuterium oxide to that of 1 mole of ordinary water yielded the value 1.031 45 ±0.000 75 for 25° C and zero pressure.

Combination of these with other data yielded the following thermodynamic values:

$D_2(g)+1/2\ O_2(g)=D_2O(liq)$, $\Delta H°_{298.16}=-294{,}563\pm94$ int. j/mole ($-70{,}414.0\pm22.5$ cal/mole), $\Delta F°_{298.16}=-243{,}470\pm100$ int. j/mole ($-58{,}200.5\pm23.9$ cal/mole);

$D_2O(liq)=D_2O(g)$, $\Delta H°_{298.16}=45{,}391\pm36$ int. j/mole ($10{,}850.5\pm8.6$ cal/mole), $\Delta F°_{298.16}=8{,}949\pm9$ int. j/mole ($2{,}139.2\pm2.2$ cal/mole);

$D_2(g)+1/2\ O_2(g)=D_2O(g)$, $\Delta H°_{298.16}=-249{,}172\pm100$ int. j/mole ($-59{,}563.5\pm23.9$ cal/mole), $\Delta F°_{298.16}=-234{,}521\pm100$ int. j/mole ($-56{,}061.2\pm23.9$ cal/mole), $\Delta H°_0=-246{,}231\pm100$ int. j/mole ($-58{,}860.5\pm23.9$ cal/mole);

$D_2(g)+H_2^1O(liq)=H_2^1(g)+D_2O(liq)$, $\Delta H°_{298.16}=-8{,}770\pm83$ int. j/mole ($-2{,}096.4\pm19.8$ cal/mole), $\Delta F°_{298.16}=-6{,}316\pm96$ int. j/mole ($-1{,}509.8\pm22.9$ cal/mole);

$D_2(g)+H_2^1O(g)=H_2^1(g)+D_2O(g)$, $\Delta H°_{298.16}=-7{,}386\pm90$ int. j/mole ($-1{,}765.6\pm21.5$ cal/mole), $\Delta F°_{298.16}=-5{,}966\pm90$ int. j/mole ($-1{,}426.1\pm21.5$ cal/mole), $\Delta H°_0=-7{,}337\pm90$ int. j/mole ($-1{,}753.9\pm21.5$ cal/mole);

$D_2O(liq)$, $S°_{298.16}=76.099\pm0.130$ int. j/degree mole (18.191 ± 0.031 cal/degree mole).

On the assumption that the bond energies in H_2^1 and D_2 are the same, and likewise in H_2^1O and D_2O, the difference in the zero-point energies of $H_2^1O(g)$ and $D_2O(g)$ was calculated to be $14{,}841\pm91$ int. j/mole ($3{,}548\pm22$ cal/mole, or $1{,}243.0\pm7.6$ wave numbers). The accord of this value with that recently calculated by Darling and Dennison from the vibrational-rotational spectra of deuterium oxide and protium oxide, $1{,}245.5\pm2.0$ wave numbers, indicates that, within the assigned limits of uncertainty, the respective bond energies are independent of the mass of the nucleus of the atom.

* Paper presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Cincinnati, Ohio, April 9–11, 1939.

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I. INTRODUCTION

It has been generally established, both experimentally and theoretically, that the various isotopes of a given chemical element differ in those properties which are functions of the mass of the nucleus, but not in those properties which are functions of the distribution of electrons about the nucleus. The greatest difference in the properties of any two isotopes is exhibited by the isotopes of hydrogen, because of the relatively large difference in mass between protium and deuterium. This relatively great difference in properties has made possible the preparation of substantially pure deuterium in large amount. Since ordinary hydrogen, oxygen, and water are substances whose properties are well known, it appeared desirable to make a calorimetric comparison of the heats of formation of ordinary liquid water and of liquid deuterium oxide from their respective elements, and of their heats of vaporization, and by appropriate thermodynamic calculations to ascertain whether the theoretical expectations and the experimental observations agree within the limits of accuracy of present-day measurements.

This paper reports the calorimetric determination of the ratio of the heats of formation of ordinary liquid water and liquid deuterium oxide, and of their heats of vaporization, and presents the results of thermodynamic calculations giving the heat and free energy of formation of deuterium oxide in the liquid and gaseous states, the heat and free energy of the reaction $D_2+H_2^1O=H_2^1+D_2O$, and the difference in the zero-point energies of H_2^1O and D_2O.

II. UNITS, MOLECULAR WEIGHTS, ETC.

The unit of energy in this work is the international joule (int. j) based upon standards of electromotive force and resistance maintained at this Bureau. Conversion to the artificial or defined calorie was made with the relation 1 cal=4.1833 int. j. The absolute tempera-

ture of the ice point was taken as 0° C= 273.16 ±0.02° K. The value of the gas constant per mole, R, was taken [2] as 8.3145 ±0.0006 absolute j/degree, or 8.3128 ±0.0008 int. j/degree, or 1.987 14 ±0.000 19 cal/degree.

On the chemical scale, the molecular weights were taken as follows: [3] H_2O, 18.0162; H^1_2O, 18.0158; H^1DO, 19.0221; D_2O, 20.0284 [1, 2, 3, 4].[4]

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [5]. In other cases, reasonable estimates of the uncertainties were made.

III. RATIO OF THE HEATS OF FORMATION OF DEUTERIUM OXIDE AND ORDINARY WATER, IN THE LIQUID STATE AT 25° C

1. METHOD AND APPARATUS

The calorimetric method used was the same as in the investigation on the heat of formation of ordinary water [6]. The reaction vessel, calorimeter, and other apparatus were also the same, except for the control of the temperature of the jacket of the calorimeter [7], the heating coil in the calorimeter [8], and the resistance thermometer and bridge [9], which had been replaced in later investigations.

2. CHEMICAL PROCEDURE

The oxygen and hydrogen, commercially prepared, were purified by passage through copper oxide and copper, respectively, each at about 600° C, Ascarite (a mixture of sodium hydroxide and asbestos), anhydrous magnesium perchlorate, and phosphorus pentoxide, in the order given.

The deuterium oxide used for preparing the gaseous deuterium for the experiments on the heat of formation has already been described [10]. The ratio of the density of the deuterium oxide to that of ordinary water at 27° C was 1.107 71, and the purity was calculated to be 1.0000 ±0.0003 mole fraction. The deuterium was prepared by passing the gaseous deuterium oxide through powdered magnesium at 480° C.[5] The purity of the deuterium as it was finally obtained under pressure in a 1-liter brass bottle was determined from measurements of vapor pressures kindly made for the authors by F. G. Brickwedde and R. B. Scott, of the Cryogenic Laboratory of this Bureau. At a temperature of 20.333° K, the vapor pressures of normal hydrogen and of the prepared deuterium, each in the liquid state, were found to be 747.34 and 253.31 mm Hg, respectively. For this same temperature, the data of Brickwedde, Scott, and Taylor [12] and of Brickwedde and Scott [13] yield 250.68 and 429.68 mm Hg, respectively, for the vapor pressures of liquid normal D_2 and liquid H^1D. Assuming from the method of preparation that the impurity in the deuterium was in equilibrium [6] with respect to the reaction $H^1_2(g)+D_2(g)=2$

[1] The derivation of these values of the constants will be discussed in a later report by one of the authors (F. D. Rossini).

[2] The chemical symbols have the following significance: H, naturally existing or normal hydrogen (consisting of 0.9998 H^1 and 0.0002 D); H^1, protium; D, deuterium, H^2; O, naturally existing or normal oxygen.

[3] Figures in brackets indicate the literature references at the end of this paper.

[4] See reference [11] for a detailed description of the method and apparatus.

[5] The assumption most contrary to this, namely, that the impurity is present entirely as molecules of H^1_2, appears to be extremely unlikely. If the calculations were carried through on this basis, the resulting value for the heat of formation of deuterium oxide would differ from that actually calculated by about 1 part in 10,000.

$H^1D(g)$ and that the value of the observed difference in vapor pressure between pure liquid D_2 and that used in this investigation was uncertain by 0.50 mm (or about 20 percent of itself), the impurity in the deuterium used was calculated to be 0.0147 ± 0.0028 mole fraction of H^1D and $0.000\,06 \pm 0.000\,01$ mole fraction of H_2^1.

The amount of reaction in the calorimetric experiments was determined from the mass of water formed in the reaction, in the manner previously described,[7] with the absorption tubes always filled with hydrogen at the times of weighing.

3. CALORIMETRIC PROCEDURE

The aim of the experimental part of this investigation was to determine as accurately as possible the ratio of the heats of formation of ordinary water and deuterium oxide, whence the value for the latter could be calculated from the value previously determined for ordinary water [6, 14, 15]. In principle, this was accomplished by determining the ratio of the masses of ordinary water and deuterium oxide whose formation produced identical rises of temperature in the same calorimeter system.

The method of reducing the actual experimental observations to this end was as follows: Let

ΔR_c = the corrected rise of temperature of the calorimeter system, expressed as the increase in resistance in ohms of the given platinum resistance thermometer at a mean temperature of 25° C, as measured on the given resistance bridge;

W = the mass of water in the given calorimeter system;

W_s = the mass of water in the "standard" calorimeter system (W will usually differ from W_s by not more than ± 10 g or $\pm 1/360$ of itself);

E_s = the energy equivalent, over a "standard" interval of temperature, of the "standard" calorimeter system, expressed as international joules per ohm increase in resistance of the given platinum resistance thermometer at a mean temperature of 25° C, as measured on the given resistance bridge;

E = the energy equivalent of the given calorimeter system containing W grams of water;

w = the mass of ordinary water formed as liquid in the reaction vessel;

w' = the mass of deuterium oxide formed as liquid in the reaction vessel;

q_{vap} = the heat of vaporization or that amount of water (ordinary or heavy) formed in the reaction but not remaining as liquid in the reaction vessel (this term corrects to the liquid state all the water formed in the reaction);

q_{gas} = the energy taken from the calorimeter by the inflowing gases;

q_{ign} = the energy added to the calorimeter by the ignition operation;

[7] See p. 6 to 9 of reference [6].

c_w = the heat capacity of 1 g of ordinary water, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer;

c'_w = the heat capacity of 1 g of deuterium oxide, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer;

m_{H_2O} = the mass of water formed in the reaction with ordinary hydrogen;

m_{D_2O} = the mass of deuterium oxide formed in the reaction with deuterium;

$(qf)_{H_2O}$ = the heat evolved, at 25° C and a constant pressure of 1 atmosphere, in the formation of 1 g of ordinary water in the liquid state from normal oxygen and hydrogen in the gaseous state; and

$(qf)_{D_2O}$ = the heat evolved, at 25° C and a constant pressure of 1 atmosphere, in the formation of 1 g of deuterium oxide in the liquid state from normal oxygen and deuterium in the gaseous state.

For the experiments with ordinary hydrogen, the following relations hold:

$$E = E_s + c_w(W - W_s + 1/2\ w) \tag{1}$$

$$m_{H_2O}(qf)_{H_2O} = (\Delta R_c)E + q_{vap} + q_{gas} - q_{ign}. \tag{2}$$

Substituting for E in eq 2, and solving for $(qf)_{H_2O}/E_s$, which will be called A_{H_2O}, there is obtained

$$A_{H_2O} = (qf)_{H_2O}/E_s =$$

$$\frac{\Delta R_c}{m_{H_2O}}\left[1 + \frac{c_w(W - W_s + 1/2\ w) + (q_{vap} + q_{gas} - q_{ign})/\Delta R_c}{E_s}\right]. \tag{3}$$

For the experiments with deuterium, the analogous equations are:

$$E = E_s + c_w(W - W_s) + c'_w(1/2\ w') \tag{4}$$

$$m_{D_2O}(qf)_{D_2O} = (\Delta R_c)E + q_{vap} + q_{gas} - q_{ign} \tag{5}$$

$$A_{D_2O} = (qf)_{D_2O}/E_s =$$

$$\frac{\Delta R_c}{m_{D_2O}}\left[1 + \frac{c_w(W - W_s) + 1/2\ c'_w w' + (q_{vap} + q_{gas} - q_{ign})/\Delta R_c}{E_s}\right]. \tag{6}$$

Then from eq 3 and 6

$$(qf)_{D_2O}/(qf)_{H_2O} = A_{D_2O}/A_{H_2O}. \tag{7}$$

If M_{H_2O} and M_{D_2O} are the molecular weights of H_2O and D_2O, respectively, then the ratio of the heats of formation, from gaseous oxygen and hydrogen or deuterium, of H_2O and D_2O in the liquid state

at 25° C and a constant pressure of 1 atmosphere, expressed in terms of the increment in heat content, ΔH, per mole, is

$$(\Delta Hf)_{D_2O}/(\Delta Hf)_{H_2O}=(A_{D_2O}/A_{H_2O})(M_{D_2O}/M_{H_2O}). \quad (8)$$

4. EXPERIMENTAL RESULTS

The data of the experiments with ordinary hydrogen and with the deuterium are given in tables 1 and 2, respectively, where the column headings are defined as above and on page 379. To the mean values of A_{H_2O} and $A_{(D_2O)^*}$ obtained from these experiments, uncertainties of 0.018 percent and 0.014 percent, respectively, were assigned, so that [9]

$$A_{H_2O}=0.103\ 508\ \pm 0.000\ 019 \text{ ohm/g} \quad (9)$$

$$A_{(D_2O)^*}=0.096\ 013\ \pm 0.000\ 013 \text{ ohm/g}. \quad (10)$$

From these values, there is obtained the ratio

$$A_{(D_2O)^*}/A_{H_2O}=0.927\ 59\ \pm 0.000\ 21. \quad (11)$$

Neglecting the minute amount of H_2^1O, the molecular weight of the $(D_2O)^*$ is

$$20.0284-(0.0147\ \pm 0.0028)(20.0284-19.0221)=20.0136\ \pm 0.0028.$$

The ratio of the molecular weights is

$$M_{(D_2O)^*}/M_{H_2O}=1.110\ 87\ \pm 0.000\ 16. \quad (12)$$

And, by eq 8, 11, and 12

$$(\Delta Hf)_{(D_2O)^*}/(\Delta Hf)_{H_2O}=1.030\ 43\ \pm 0.000\ 28. \quad (13)$$

TABLE 1.—*Calorimetric data of the experiments on the heat of formation of ordinary water* [a, b]

Experiment number [a]	k	K	U	ΔR_c	W	q_{vap}	q_{gas}	q_{ign}	m_{H_2O}	A_{H_2O}	Deviation from mean
	1/min	*Ohms*	*Ohms*	*Ohms*	*g*	*Joules*	*Joules*	*Joules*	*g*	*Ohms/g*	*Ohms/g*
1	0.001 872	0.003 797	−0.000 120	0.300 460	3615.33	67.8	1.0	7.5	2.903 42	0.103 531	0.000 023
2	.001 905	.003 844	.000 022	.299 316	3623.11	67.1	1.6	7.5	2.896 70	.103 565	.000 057
3	.001 894	.003 152	−.000 008	.251 031	3615.67	51.7	0.8	7.5	2.426 24	.103 497	−.000 011
4	.001 875	.003 098	.000 082	.250 485	3619.09	47.6	3.6	7.5	2.422 47	.103 526	.000 016
5	.001 870	.003 123	.000 030	.250 633	3618.66	52.2	2.4	7.5	2.424 92	.103 480	−.000 028
6	.001 856	.003 048	.000 020	.250 217	3614.87	58.8	0.7	7.5	2.418 17	.103 504	−.000 004
7	.001 879	.003 183	−.000 018	.249 375	3609.63	53.2	3.2	7.5	2.406 66	.103 494	−.000 014
8	.001 874	.003 141	−.000 032	.247 892	3620.46	52.9	0.8	7.5	2.398 92	.103 507	−.000 001
9	.001 911	.003 123	.000 084	.248 798	3619.54	60.1	2.4	7.5	2.408 52	.103 469	−.000 039
Mean										0.103 508	
Standard deviation of the mean [5]										±0.000009	

[a] The results of 2 other experiments made in this series are not included, because their deviations from this mean were, respectively, about 6 and 8 times the normal deviation for such experiments.

[b] See text on p. 372 for explanation of symbols.

[9] The symbol $(D_2O)^*$ is used to denote the actual deuterium oxide, which, in the experiments on formation, was formed from deuterium that contained 0.0147 ±0.0028 mole fraction of H^1D and 0.000 06 ±0.000 01 mole fraction of H_2^1 (see section III-2).

TABLE 2.—*Calorimetric data of the experiments on the heat of formation of deuterium oxide* [a]

Experiment number	k	K	U	ΔR_c	W	q_{vap}	q_{gas}	q_{ign}	m_{D_2O}	$A_{(c_{D_2O})^*}$	Deviation from mean
	1/min	*Ohms*	*Ohms*	*Ohms*	*g*	*Joules*	*Joules*	*Joules*	*g*	*Ohms/g*	*Ohms/g*
1	0.001 916	0.004 081	−0.000 066	0.245 183	3619.61	53.3	2.5	7.5	2.556 57	0.096 034	+0.000 021
2	.001 877	.002 774	.000 070	.250 078	3621.70	57.2	1.2	7.5	2.610 41	.096 005	−.000 008
3	.001 891	.002 689	.000 052	.251 528	3620.47	45.7	2.9	7.5	2.623 57	.096 020	+.000 007
4	.001 975	.002 845	.000 200	.248 997	3616.96	39.6	1.7	7.5	2.595 13	.095 987	−.000 026
5	.001 888	.002 813	.000 156	.250 733	3623.51	46.6	1.5	7.5	2.617 46	.096 018	+.000 005
6	.001 886	.003 289	.000 048	.211 428	3619.94	49.0	1.0	7.5	2.205 59	.096 013	.000 000
Mean										0.096 013	
Standard deviation of the mean [5]										±0.000006	

[a] See text on p. 372 for explanation of symbols.

With an approximate value for the difference in the heats of formation of D_2O and H^1DO, one can correct the value for $(D_2O)^*$ for the small amount of H^1DO in it and obtain a value for the heat of formation of pure D_2O. By the method discussed in section VI–5, it was calculated that, for the formation of liquid water from gaseous normal oxygen and the given hydrogen at 25° C,

$$(\Delta Hf)_{D_2O} - (\Delta Hf)_{H^1DO} = -4{,}700 \pm 900 \text{ int. j/mole.} \quad (14)$$

In a similar manner, it was calculated that

$$(\Delta Hf)_{H^1DO} - (\Delta Hf)_{H_2^1O} = -4{,}070 \pm 900 \text{ int. j/mole.} \quad (15)$$

The foregoing calculations were made by taking the heat of vaporization of liquid H^1DO at 25° C to be 44,700 ±200 int. j/mole, the value of $H^\circ_{298.16} - H^\circ_0$ to be 8,519 ±8 int. j/mole for $H^1D(g)$ and 9,930 ±12 int. j/mole for $H^1DO(g)$, and the difference in the zero-point energies between $H_2^1(g)$ and $H^1D(g)$ and between $H_2^1O(g)$ and $H^1DO(g)$ to be 3,419 ±12 and 7,400 ±900 int. j/mole, respectively. The value for the heat of formation of liquid ordinary water, from gaseous normal hydrogen and oxygen, at 25° C, has already been reported [15] to be

$$(\Delta Hf)^\circ_{H_2O} = -285{,}795 \pm 40 \text{ int. j/mole.} \quad (16)$$

Taking account of the 0.0147 mole fraction of H^1DO in the D_2O, it was calculated that

$$(\Delta Hf)_{D_2O} - (\Delta Hf)_{(D_2O)^*} = -70 \pm 13 \text{ j/mole.} \quad (17)$$

Or, in terms of $(\Delta Hf)_{H_2O}$,

$$(\Delta Hf)_{D_2O} - (\Delta Hf)_{(D_2O)^*} = (0.000\,25 \pm 0.000\,05)(\Delta Hf)_{H_2O}. \quad (18)$$

Combination of eq 13 and 18 yields

$$(\Delta Hf)_{D_2O} = (1.030\,68 \pm 0.000\,29)(\Delta Hf)_{H_2O}, \text{ or} \quad (19)$$

$$(\Delta Hf)_{D_2O} - (\Delta Hf)_{H_2O} = -8{,}768 \pm 83 \text{ int. j/mole.} \quad (20)$$

Taking account, in a similar manner, of the 0.0004 mole fraction o
H^1DO in H_2O, it was calculated that

$$(\Delta Hf)_{H^1_2O} - (\Delta Hf)_{H_2O} = 1.6 \pm 0.4 \text{ j/mole.} \quad (21)$$

Or, in terms of $(\Delta Hf)_{H_2O}$,

$$(\Delta Hf)_{H^1_2O} = (0.999\,994 \pm 0.000\,002)(\Delta Hf)_{H_2O}. \quad (22)$$

Therefore,

$$(\Delta Hf)_{D_2O} = (1.030\,68_8 \pm 0.000\,29_0)(\Delta Hf)_{H^1_2O}. \quad (23)$$

Assuming the conversion from a real pressure of 1 atmosphere t
the hypothetical standard state with fugacity equal to 1 atmospher
to be the same (−3.6 j/mole [15] for the formation of the differen
species of water, the following values were obtained:

$$H_2(g) + 1/2O_2(g) = H_2O(liq);\ \Delta H°_{298.16} = -285{,}795 \pm 40 \text{ int. j/mole} \quad (24)$$

$$H^1_2(g) + 1/2O_2(g) = H^1_2O(liq);\ \Delta H°_{298.16} = -285{,}793 \pm 40 \text{ int. j/mole} \quad (25)$$

$$D_2(g) + 1/2O_2(g) = D_2O(liq);\ \Delta H°_{298.16} = -294{,}563 \pm 94 \text{ int. j/mole} \quad (26)$$

IV. RATIO OF THE HEATS OF VAPORIZATION OF DEU TERIUM OXIDE AND ORDINARY WATER, AT 25° C

1. METHOD AND APPARATUS

The calorimetric method used in these experiments was substan
tially the same as that previously used in this laboratory to determin
the change in internal energy of gases as a function of the pressure [33]
in which experiments the change of state was from that of a gas at
high pressure (20 to 40 atmospheres) to that of a gas at a pressure o
1 atmosphere. In the experiments on vaporization, the change o
state was from that of a liquid under its own vapor pressure to tha
of a gas at a low pressure (about 2 mm Hg).

The calorimetric apparatus for the experiments on the heat o
vaporization was the same as for the experiments on the heat of for
mation, except that the reaction vessel (see fig. 2 of reference [6]) wa
replaced by the one shown in figure 1 of this paper.

2. CHEMICAL PROCEDURE

In the case of both the ordinary water and the deuterium oxide, al
transfer of material was effected in the absence of air by distilling th
material under its own vapor pressure at room or lower temperature
The experiments with ordinary water were performed first, followe
by those with deuterium oxide. Before receiving deuterium oxide
the entire system, including vessels and connecting tubes, was twic
flushed with the vapor of deuterium oxide and evacuated.

The deuterium oxide was removed from its sealed glass ampoule b
placing the latter inside a second glass tube connected, as shown i

figure 1, to a receiving vessel; evacuating the entire system; placing liquid air around the tube containing the sealed glass ampoule; letting the latter break as a result of the expansion of the deuterium oxide on freezing; replacing the liquid air with water at room temperature; flushing and evacuating the system twice; placing a refrigerant at about −80° C (solid carbon dioxide in a mixture of carbon tetrachloride and chloroform) around the receiving bulb; and permitting the distillation to proceed at the vapor pressure of the deuterium oxide at room temperature. The deuterium oxide was then transferred in a similar manner to the reaction vessel.

For the experiments with ordinary water, distilled water from the Bureau's Chemistry Building supply line was used, with dissolved air removed by the distillation process described above.

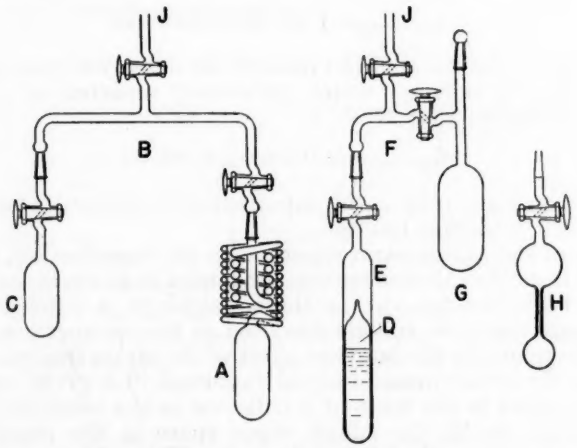

FIGURE 1.—*Apparatus (glass) used in the experiments on vaporization.*

A, calorimetric reaction vessel from which water is vaporized; *B*, connecting tube; *C*, receiving bulb; *J*, connection to vacuum pump; *D*, sealed ampoule containing original deuterium oxide; *E*, bulb in which the ampoule of deuterium oxide is broken; *F*, connecting tube; *G*, reservoir; *H*, picnometer for determining densities "in vacuo."

The deuterium oxide used in the experiments on vaporization was a lot of 25 g obtained commercially,[9] which was sealed in a glass ampoule and labeled "99.9+ percent deuterium oxide." The purity of this material was determined at the conclusion of the experiments on vaporization by measuring at 27.00° C the ratio of the mass of it to the mass of ordinary water required to fill to a given mark the picnometer shown in figure 1. In the determination of the specific gravity of the deuterium oxide, the material was transferred entirely in the absence of air, by distillation at its own vapor pressure at room temperature, with the deuterium oxide and the ordinary water being at all times in contact only with their respective vapors. In weighing

[9] This deuterium oxide was purchased from the Stuart Oxygen Co., San Francisco, Calif.

the picnometer, a duplicate of it was used as a counterpoise, and correction was made for the buoyant effect of the air on the brass weights. If d is the density and m is the mass of liquid required to fill the picnometer to the given volume, then [10]

$$d_{(D_2O)^*}/d_{H_2O}=m_{(D_2O)^*}/m_{H_2O} \tag{27}$$

To obtain the actual mass of liquid in the picnometer, there was subtracted from the total mass of water (liquid plus vapor) in the picnometer the mass of the water vapor in the space above the liquid. This correction amounted to 0.001 39 g for the ordinary water, and correspondingly to 0.001 35 g for the deuterium oxide. The total volume of the liquid in the picnometer was near 16.8 ml. The measurements yielded, for 27.00° C, the value

$$d_{(D_2O)^*}/d_{H_2O}=1.107\ 84\ \pm 0.000\ 16 \tag{28}$$

On the basis of the value of the ratio of the density of pure deuterium oxide to that of ordinary water, previously reported by one of the authors [10], namely, for 27.00° C,

$$d_{D_2O}/d_{H_2O}=1.107\ 69\ \pm 0.000\ 05 \tag{29}$$

the deuterium oxide used in the vaporization experiments had a purity of 1.0000 ±0.0015 mole fraction.

In each of the calorimetric experiments on vaporization, the liquid vaporized from the calorimeter was condensed in an evacuated weighed receiving bulb (see fig. 1). In these weighings, a duplicate bulb of substantially the same volume was used as the counterpoise, and correction was made for the buoyant effect of the air on the brass weights. To obtain the actual mass of liquid vaporized in a given experiment, there was added to the mass of it collected in the receiving bulb that mass required to fill the added vapor space in the reaction vessel caused by the removal of liquid from it. This added mass of water was calculated from the densities of the liquid and vapor phases at 25° C to be 0.000 02_3 g of vapor per gram of liquid for H_2O, and correspondingly to 0.000 02_0 g of vapor per gram of liquid for D_2O.

3. CALORIMETRIC PROCEDURE

In the calorimetric experiments, the water under investigation was vaporized from the calorimetric reaction vessel by lowering the vapor pressure of the water in the receiving bulb outside the calorimeter through control of its temperature. The pressure in the reaction vessel in the calorimeter was constant at the value water normally has at 25° C, namely, about 24 and 21 mm Hg for ordinary water and deuterium oxide, respectively. The temperature of the jacket of the calorimeter was maintained constant, and, during the actual vaporization of water, electric energy was given to the calorimeter at a rate that substantially balanced the rate of withdrawal of energy by vaporization. Having once determined approximately the electric power required, this was kept constant, and necessary slight variations in the rate of vaporization were effected by changing the effective

[10] $(D_2O)^*$ represents the actual deuterium oxide used.

temperature of the receiving bulb through alteration of its depth of immersion in the refrigerant (solid carbon dioxide in a mixture of carbon tetrachloride and chloroform).

The times of the "fore," "reaction," and "after" periods in the calorimetric experiments were 20, 70, and 20 minutes, respectively, with the actual vaporization occurring in the first 60 minutes of the 70-minute "reaction" period. The substantially constant rate of input of energy to the calorimeter through stirring, etc., u, measured in ohms per minute, was taken as the average of the values calculated for this quantity from the observations of the "fore" and "after" periods. The value of the heat-leak constant, k, was taken as 0.00198/min. a value determined in other experiments with larger differences of temperature between the jacket and the calorimeter can.

During the reaction period, the energy removed from the calorimeter by the vaporization process, is

$$Q=(\text{electric energy})-E(\Delta R-U-K), \tag{30}$$

where the electric energy is in int. j; E is the energy equivalent of the calorimeter system in int. j/ohm; ΔR is the increase in resistance, in ohms, of the platinum resistance thermometer during the reaction period; U is the product of u and the time of the reaction period; and K is the product of k, the time of the reaction period, and $(R_j-R_c)_{ave}$, the average, with respect to time, of the difference in temperature between the jacket and the calorimeter expressed in ohms on the given platinum resistance thermometer.

If m is the mass of water vaporized, then the heat of vaporization of 1 g of water, from a liquid under its own vapor pressure to a gas issuing from the exit end of the calorimeter at the given pressure and velocity, is

$$l_v=Q/m, \tag{31}$$

where Q is given by eq 30.

To reduce the heat content of the gas to zero pressure with no directed kinetic energy, there must be added to the above value of l_v the increase in the heat content of the gas in going to zero pressure from the pressure at the exit end of the calorimeter, and there must be subtracted from it the amount of directed kinetic energy possessed by the gas as it issued from the calorimeter. For the former correction, the value of $(dH/dP)_T$ is taken to be the same, per mole, for both ordinary water vapor and deuterium oxide vapor, namely, 705 $\pm$35 j/atm mole [15]. This correction was calculated to be 0.10 and 0.09 j/g for ordinary water and deuterium oxide, respectively, under the given conditions. The pressure of the gas at the exit end of the calorimeter was calculated, from the known dimensions of the path of travel of the vapor and the total known pressure drop from the reservoir in the reaction vessel to the receiving vessel outside the calorimeter, to be 1.9_8 and 1.7_2 mm Hg for the ordinary water and the deuterium oxide, respectively. From the pressure, the cross-sectional area at the exit end of the calorimeter, and the known rate of with-

drawal of water from the reaction vessel, the directed kinetic energy was calculated to be 0.61 and 0.59 j/g for the ordinary water and the deuterium oxide, respectively.

4. EXPERIMENTAL RESULTS

The experimental data obtained on the vaporization of ordinary water are given in table 3 and those for deuterium oxide in table 4. The final over-all uncertainty of each value, obtained by including uncertainties in the small corrections to zero pressure and for directed kinetic energy equal to 100 percent of their own values, is given in the last line of each table.

TABLE 3.—*Calorimetric data on the heat of vaporization of ordinary water* [a]

Experiment number	Electric energy	ΔR	U	K	Energy equivalent of calorimeter	Mass of H_2O	Average temperature	Heat of vaporization [b] at 25° C	Deviation from mean
	Int. j	*Ohms*	*Ohms*	*Ohms*	*Int. j/ohm*	*g*	*° C*	*Int. j/g*	*j/g*
1	22, 406. 6	−0. 004 158	0. 000 762 2	0. 000 691 6	147, 460	9. 495 99	24. 95	2446. 11	2. 07
2	22, 398. 8	. 002 690	. 000 770 0	. 000 189 9	147, 084	9. 061 56	24. 98	2443. 20	−0. 84
3	23, 123. 0	−. 001 864	. 000 805 0	−. 000 221 8	147, 609	9. 608 57	25. 02	2443. 63	−. 41
4	23, 141. 6	. 002 066	. 000 798 0	−. 000 140 0	147, 215	9. 385 08	25. 01	2443. 21	−. 83
Mean								2444. 04	
Standard deviation of the mean [5]								±0. 70	
Uncertainty interval [c] [5]								±1. 52	

[a] See text on p. 379 for explanation of symbols.
[b] Corrected to 25.00° C (taking $dl/dT = -2.36$ j/g degree), to zero directed kinetic energy (−0.61 j/g), and to zero pressure (+0.10 j/g).
[c] Including assumed uncertainties of 100 percent of the values of the corrections given in footnote b.

TABLE 4.—*Calorimetric data on the heat of vaporization of deuterium oxide* [a]

Experiment number	Electric energy	ΔR	U	K	Energy equivalent of calorimeter	Mass of D_2O	Average temperature	Heat of vaporization [b] at 25° C	Deviation from mean
	Int. j	*Ohms*	*Ohms*	*Ohms*	*Int. j/ohm*	*g*	*° C*	*Int. j/g*	*j/g*
1	20, 161. 0	−0. 001 905	0. 000 615 6	0. 000 046 6	147, 429	9. 052 67	25. 01	2268. 41	0. 76
2	20, 148. 6	. 000 993	. 000 574 0	. 000 123 4	147, 064	8. 861 84	25. 00	2268. 23	. 58
3	19, 728. 9	−. 002 623	. 000 503 2	−. 000 177 3	147, 319	8. 889 67	25. 02	2267. 72	. 07
4	19, 705. 8	. 001 971	. 000 406 0	. 000 011 1	146, 962	8. 592 79	25. 01	2266. 23	−1. 42
Mean								2267. 65	
Standard deviation of the mean [5]								±0. 50	
Uncertainty interval [c] [5]								±1. 17	

[a] See text on p. 379 for explanation of symbols.
[b] Corrected to 25.00° C (taking $dl/dT = -2.36$ j/g degree), to zero directed kinetic energy (−0.59 j/g), and to zero pressure (+0.09 j/g).
[c] Including assumed uncertainties of 100 percent of the values of the corrections given in footnote b.

The value obtained from the present experiments for the heat of vaporization of ordinary water to zero pressure, namely, 2444.04 ±1.52 int. j/g at 25° C, agrees, within the respective limits of uncer-

tainty, with the value obtained by converting the recent data of Osborne, Stimson, and Ginnings [34] (which were obtained at saturation pressure) to zero pressure, which value is 2442.63 ±0.72 int. j/g at 25° C [15].

The calorimeter used in the present experiments on vaporization was not especially designed for measuring heats of vaporization (in particular, it was designed to transfer energy at the rate of 50 to 150 watts, whereas in the experiments on vaporization the rate of transfer of energy was less than 7 watts), and there is the possibility of the existence of some small unaccounted-for constant errors. Therefore, it is felt that, from the data of the present experiments on vaporization, there can be obtained a value for the ratio of the heats of vaporization of deuterium oxide and ordinary water that is more accurate than the value for either one separately, and that a "best" value for the difference in their heats of vaporization and for the heat of vaporization of deuterium oxide can be obtained by combining this ratio with the "best" value for the heat of vaporization of ordinary water, as obtained from the data of Osborne, Stimson, and Ginnings [34], plus a correction to zero pressure [15].

The present data yield for the ratio of the heat of vaporization of 1 g of ordinary water to that of 1 g of deuterium oxide, to zero pressure at 25° C, the value

$$l^\circ_{H_2O}/l^\circ_{D_2O}=1.077\ 79\ \pm 0.000\ 78. \tag{32}$$

Combination of this ratio with the ratio of the molecular weights of D_2O and H_2O,

$$M_{D_2O}/M_{H_2O}=1.111\ 69 \tag{33}$$

yields for the ratio of the molal heats of vaporization, to zero pressure at 25° C,

$$L^\circ_{D_2O}/L^\circ_{H_2O}=1.031\ 45\ \pm 0.000\ 75. \tag{34}$$

For the heat of vaporization of ordinary water, the following "best" value has already been reported [15]:

$$H_2O(liq)=H_2O(g);\ \Delta H^\circ_{298.16}=44{,}007\ \pm 13\ \text{int. j/mole}. \tag{35}$$

Combination of eq 34 and 35 yields for the difference in the heats of vaporization of deuterium oxide and ordinary water at 25° C

$$L^\circ_{D_2O}-L^\circ_{H_2O}=1{,}384\ \pm 33\ \text{int. j/mole}, \tag{36}$$

and for the heat of vaporization of deuterium oxide to zero pressure at 25° C

$$D_2O(liq)=D_2O(g);\ \Delta H^\circ_{298.16}=45{,}391\ \pm 36\ \text{int. j/mole}. \tag{37}$$

The difference in the heats of vaporization of H_2O and H_2^1O would be expected to be quite negligible—of the order of 0.2 j/mole.

V. COMPARISON WITH PREVIOUS EXPERIMENTAL DATA

1. HEAT OF FORMATION OF LIQUID DEUTERIUM OXIDE

In 1935, Flood and Tronstad [28] reported the results of experiments on the determination of the ratio of the heat of formation of liquid deuterium oxide to that of ordinary water. The following is descriptive of their experimental work: In each experiment, they exploded about 18 cm^3 (measured at 1 atmosphere) of "Knallgas" ($D_2+1/2O_2$ or $H_2+1/2O_2$); the volume of the explosion vessel was 100 cm^3; the temperature rise was of the order of 3.9° C; about 5 percent of the water formed in the reaction remained as vapor in the explosion vessel, and this amount was corrected to the liquid state; the average temperature of the reaction was about 17° C; about 0.0005 mole of deuterium (or of ordinary hydrogen) was burned in each of the experiments. This last figure is to be compared with the approximately 0.13 mole of deuterium burned in each of the six experiments of the present investigation. For the ratio of the heat of formation of liquid deuterium oxide to that of liquid ordinary water, Flood and Tronstad reported 1.027 ± 0.003, without giving the numerical details of their work or the manner of estimating the uncertainty. Within its assigned limits of uncertainty, this value is in substantial accord with the value $1.030\,68 \pm 0.000\,29$ obtained in the present investigation (eq 19).

2. HEAT OF VAPORIZATION OF DEUTERIUM OXIDE

A value for the heat of vaporization of deuterium oxide may be deduced from the calorimetric measurements of Bartholomé and Clusius [17] on the heat of sublimation of deuterium oxide at 0° C and those of Long and Kemp [16] on the heat of fusion of deuterium oxide at 3.82° C, together with appropriate heat-capacity data for conversion to 25° C. The data to be combined are the following:

$$D_2O(c) = D_2O(g);\ \Delta H^\circ_{273.16} = 52{,}996 \pm 110 \text{ int. j/mole} \quad (38)$$

$$D_2O(c) = D_2O(liq);\ \Delta H^\circ_{276.98} = 6{,}279 \pm 15 \text{ int. j/mole} \quad (39)$$

$$D_2O(liq);\quad H^\circ_{298.16} - H^\circ_{276.98} = 1{,}770 \pm 3 \text{ int. j/mole} \quad (40)$$

$$D_2O(c);\quad H^\circ_{276.98} - H^\circ_{273.16} = 172 \pm 1 \text{ int. j/mole} \quad (41)$$

$$D_2O(g);\quad H^\circ_{298.16} - H^\circ_{273.16} = 852 \pm 3 \text{ int. j/mole.} \quad (42)$$

The values for eq 39, 40, and 41 were calculated from the data of Long and Kemp [16], who measured the heat of fusion of deuterium oxide and its heat capacity in the liquid and solid states (see also references [30, 31, 32]). The value for eq 42 was calculated statistically, the vibrational energy contribution being found to be 20.8 j/mole. The value for eq 38 was calculated from the data of Bartholomé and Clusius [17], who measured the heat of sublimation of D_2O at 0° C in a Bunsen ice calorimeter. Their data yield 9.7604 g of mercury displaced for each gram of deuterium oxide sublimed, the total in three experiments being 12.5714 g of mercury displaced and 1.2880 g of deuterium oxide sublimed. Taking as the energy equivalent of the Bunsen ice calorimeter 271.10 int. j/g of mercury displaced [18], the data of Bartholomé and Clusius yield 52,996 int. j/mole for the heat of the reaction given by eq 38. Combination of eq 35, 38,

39, 40, 41, and 42 yields 1,620 ±112 int. j/mole for the difference in the heats of vaporization of deuterium oxide and ordinary water at 25° C.

The data of Miles and Menzies [19], who measured the difference between the vapor pressures of deuterium oxide and of ordinary water as a function of the temperature over the range from 25° to 230° C, yield 1,324 ±135 int. j/mole for the difference in the heats of vaporization at 25° C.

The less extensive data of Lewis and MacDonald [20] on the difference in the vapor pressures as a function of the temperature over the range from 20° to 110° C yield 1,140 ±150 int. j/mole for the difference in the heats of vaporization.

The three values just given for the difference between the heats of vaporization of deuterium oxide and of ordinary water, namely, 1,620 ±112, 1,324 ±135, and 1,140 ±150 int. j/mole, are to be compared with the value 1,384 ±33 int. j/mole determined in the present investigation.

VI. THERMODYNAMIC CALCULATIONS

1. HEAT OF FORMATION OF DEUTERIUM OXIDE AT 25° C AND 0° K

Values for the heat of formation of gaseous ordinary water at 25° C and 0° K have already been reported [11] [15]:

$$H_2(g)+1/2O_2(g)=H_2O(g) \tag{43}$$

$$\Delta H^\circ_{298.16}=-241{,}788 \pm 42 \text{ int. j/mole} \tag{44}$$

$$\Delta H^\circ_0=-238{,}896 \pm 42 \text{ int. j/mole} \tag{45}$$

The corresponding values for deuterium oxide may be obtained by combining eq 20, 24, and 36 (or 26 and 37) and the values for $H^\circ_{298.16}-H^\circ_0$ given in table 5 for $D_2(g)$, $D_2O(g)$, and $O_2(g)$:

$$D_2(g)+1/2O_2(g)=D_2O(g) \tag{46}$$

$$\Delta H^\circ_{298.16}=-249{,}172 \pm 100 \text{ int. j/mole} \tag{47}$$

$$\Delta H^\circ_0=-246{,}231 \pm 100 \text{ int. j/mole} \tag{48}$$

2. FREE ENERGY OF FORMATION OF DEUTERIUM OXIDE AT 25° C

The entropies given in table 5 may be appropriately combined with the heat of formation to obtain the free energy of formation, according to the relation

$$\Delta F=\Delta H-T\Delta S. \tag{49}$$

In this way there was obtained

$$D_2(g)+1/2O_2(g)=D_2O(g);\Delta F^\circ_{298.16}=-234{,}521 \pm 100 \text{ int. j/mole} \tag{50}$$

[11] The values used in this paper for $\Delta F^\circ_{298.16}$ and ΔH°_0 for the formation $H_2O(g)$, according to eq 43, differ from those given in reference [15] by −9 and 4 j/mole, respectively, because of slight improvements in the accuracy of the values calculated by one of the authors [25] for $S^\circ_{298.16}$ and $H^\circ_{298.16}-H^\circ_0$ for $H_2O(g)$. These changes are almost negligible, however, being only one-fifth and one-tenth, respectively, of the assigned uncertainties.

TABLE 5.—*Summary of values of the entropy (not including nuclear spin) at 25° C, and of the heat content at 25° C referred to 0° K*

Substance	$S°_{298.16}$		$H°_{298.16}-H°_0$		Sources of data
	Int. j/deg mole	*cal [a]/deg mole*	*Int j/mole*	*cal [a]/mole*	
O_2(g)	205.090 ±0.040	49.026 ±0.010	8653.6 ±3.0	2068.6 ±0.7	[15, 26]
H_2(g)	130.644 ±0.020	31.230 ±0.005	8466.6 ±2.0	2023.9 ±0.5	[15, 25, 27]
H_2O (g)	188.813 ±0.040	45.135 ±0.010	9901.3 ±3.0	2366.9 ±0.7	[15, 26]
H_2O (liq)	70.081 ±0.080	16.752 ±0.019			[15]
D_2(g)	144.914 ±0.040	34.641 ±0.010	8568.7 ±3.0	2048.3 ±0.7	[c] [23]
D_2O(g)	198.322 ±0.040	47.408 ±0.010	9954.0 ±3.0	2379.5 ±0.7	[16]
D_2O(liq)	76.099 ±0.130	18.191 ±0.031			[b]

[a] The calorie is defined as 4.1833 int. j.
[b] See eq 54.
[c] The values of the entropies (including nuclear spin) of D_2 and HD given in table 4 of reference [25] are recorded incorrectly for T=298.1°K. The correct values are, respectively, 39.001 and 37.919. The entries for the other temperatures are correct (H. L. Johnston).

From the data of Miles and Menzies [19] (see also Lewis and MacDonald [20]), the vapor pressure of liquid deuterium oxide at 25° C may be taken as 3.15 ±0.05 mm Hg less than that of ordinary water. With the vapor pressure of ordinary water taken as 0.031 222 ±0.000 020 atmosphere at 25° C [21], the vapor pressure of liquid deuterium oxide at 25° C becomes 0.027 08 ±0.000 07 atmosphere. Assuming $d(F_{ideal}-F_{real})/dP$ at 25° C to be the same for D_2O(g) as for H_2O(g), namely, 150 ±40 j/atm mole [15], there is obtained

$$D_2O(liq)=D_2O(g)\ ;\ \Delta F°_{298.16}=8{,}949\tfrac{1}{2}\pm 9 \text{ int. j/mole.} \quad (51)$$

Combination of eq 50 and 51 yields

$$D_2(g)+1/2O_2(g)=D_2O(liq)\ ;\ \Delta F°_{298.16}=-243{,}470\ \pm 100 \text{ int. j/mole.} \quad (52)$$

3. ENTROPY OF LIQUID DEUTERIUM OXIDE AT 25° C

Combination of eq 37, 49, and 51 yields

$$D_2O(liq)=D_2O(g)\ ;\ \Delta S°_{298.16}=122.223\ \pm 0.124 \text{ int. j/degree mole.} \quad (53)$$

Combination of eq 53 with the entropy of D_2O(g) given in table 5 yields

$$D_2O(liq)\ ;\ S°_{298.16}=76.099\ \pm 0.130 \text{ int. j/degree mole.} \quad (54)$$

4. THE REACTION $D_2+H_2^1O=H_2^1+D_2O$

The data on the heats and free energies of formation of ordinary water and deuterium oxide were combined to give the following values for the isotopic exchange reaction:

$$D_2(g)+H_2^1O(liq)=H_2^1(g)+D_2O(liq). \quad (55)$$

$$\Delta H°_{298.16}=-8{,}770\ \pm 83 \text{ int. j/mole.} \quad (56)$$

$$\Delta F°_{298.16}=-6{,}316\ \pm 96 \text{ int. j/mole.} \quad (57)$$

$$D_2(g)+H_2^1O(g)=H_2^1(g)+D_2O(g). \quad (58)$$

$$\Delta H°_{298.16}=-7{,}386\ \pm 90 \text{ int. j/mole.} \quad (59)$$

$$\Delta F°_{298.16}=-5{,}966\ \pm 90 \text{ int. j/mole.} \quad (60)$$

$$\Delta H°_0=-7{,}337\ \pm 90 \text{ int. j/mole.} \quad (61)$$

It should be noted that the above values are significantly different from those reported in the literature. For example, for the isotopic exchange reaction in the gaseous phase as given by eq 58, the calculations of Jones and Sherman [29] give

$$\Delta H_0^\circ = -1{,}488 \text{ cal/mole}; \; K_{298.16} = 7.088, \tag{62}$$

which values are to be compared with

$$\Delta H_0^\circ = -1{,}754 \pm 22 \text{ cal/mole}; \; K_{298.16} = 11.10 \pm 0.42 \tag{63}$$

from the present work.[12]

5. ZERO-POINT ENERGIES

If the energy of binding of atoms is the same for different isotopes of the same element, that is, dependent on the electron distribution about the nucleus but independent of the mass of the nucleus, then the differences in the heats of formation of D_2O and H_2^1O at 0° K, as given by eq 26, 28, 35, and 37, will be equal to the appropriate differences in the zero-point energies of the molecules concerned. If $(\Delta Hf_0^\circ)_{H_2^1O}$ and $(\Delta Hf_0^\circ)_{D_2O}$ represent, respectively, the heats of formation of H_2^1O and D_2O from their elements at O° K, as given by the equations just cited, and ZPE represents the zero-point energy, then, on the assumption just mentioned,

$$(\Delta Hf_0^\circ)_{H_2^1O} - (\Delta Hf^\circ{}_0)_{D_2O} = [(ZPE)_{H_2^1O} - (ZPE)_{D_2O}] - [(ZPE)H_2^1 - (ZPE)_{D_2}]. \tag{64}$$

Values of the zero-point energies of H_2 and D_2 are accurately known from the spectroscopic data of Teal and MacWood [22], which are in substantial agreement with the data of Jeppeson [23]. Expressed in terms of wave numbers (in cm)$^{-1}$ the zero-point energies of H_2^1 and D_2 are, respectively, 2171.3_5 and 1542.8_6, the difference being 628.5 wave numbers. Converted to international joules by means of the factor 11.940, these values become, respectively, 25,926, 18,422, and 7,504 int. j/mole. The uncertainty in the difference may be conservatively placed at ±12 j/mole. Then

$$(ZPE)_{H_2^1} - (ZPE)_{D_2} = 7{,}504 \pm 12 \text{ int. j/mole}. \tag{65}$$

From eq 61,

$$(\Delta Hf_0^\circ)_{H_2^1O} - (\Delta Hf_0^\circ)_{D_2O} = 7{,}337 \pm 90 \text{ int. j/mole}. \tag{66}$$

Therefore, from eq 64, 65, and 66

$$(ZPE)_{H_2^1O} - (ZPE)_{D_2O} = 14{,}841 \pm 91 \text{ int. j/mole} = 3{,}548 \pm 22 \text{ cal/mole} = 1243.0 \pm 7.6 \text{ wave numbers}. \tag{67}$$

An extensive analysis of the data on the vibrational-rotational spectra of the H_2^1O and D_2O molecules has just been completed by Darling and Dennison [35], who have developed a new theory of the water molecule in connection with the problem of expressing the

[12] K is defined by the relation $\Delta F^\circ = -RT\ln K$, and, for the isotopic exchange reaction under consideration, at pressures sufficiently low for the fugacity to be replaced by the partial pressure $K = (P_{D_2O} P_{H_2^1}) / (P_{H_2^1O} P_{D_2})$

energies of the various levels of the molecule in terms of certain constants evaluated from their equation and the spectroscopic data. They find that, for those states where resonance may be neglected, of which the ground state is one, the energy, W, of a given level is given by the equation

$$W/hc=\omega_1(n_1+1/2)+\omega_2(n_2+1/2)+\omega_3(n_3+1/2)+X_{11}(n_1+1/2)^2+X_{22}(n_2+1/2)^2+X_{33}(n_3+1/2)^2+X_{12}(n_1+1/2)(n_2+1/2)+X_{13}(n_1+1/2)(n_3+1/2)+X_{23}(n_2+1/2)(n_3+1/2), \quad (68)$$

where ω_1, ω_2, and ω_3 are the normal frequencies, n_1, n_2, and n_3 are the quantum numbers for the three different modes of vibration, and the X's are the interaction coefficients. Darling and Dennison [35] obtain the following values for the constants, with the energy expressed in wave numbers:

	H_2^1O	D_2O
ω_1	3825.32	2758.06
ω_2	1653.91	1210.25
ω_3	3935.59	2883.79
X_{11}	−43.89	−22.81
X_{22}	−19.50	−10.44
X_{33}	−46.37	−24.90
X_{12}	−20.02	−10.56
X_{13}	−155.06	−81.92
X_{23}	−19.81	−10.62

The zero-point energy of the molecule is given by eq 68 with $n_1=n_2=n_3=0$, as follows:

$$ZPE=1/2(\omega_1+\omega_2+\omega_3)+1/4(X_{11}+X_{22}+X_{33}+X_{12}+X_{13}+X_{23}). \quad (69)$$

On substitution of the constants in eq 69, Darling and Dennison obtain the following values for the zero-point energies:

$$(ZPE)_{H_2^1O}=4631.25 \text{ wave numbers.} \quad (70)$$

$$(ZPE)_{D_2O}=3385.74 \text{ wave numbers.} \quad (71)$$

$$(ZPE)_{H_2^1O}-(ZPE)_{D_2O}=1245.51 \text{ wave numbers.} \quad (72)$$

Dennison, in a private communication to the authors, has placed an uncertainty of 2 wave numbers on the above value for the difference in the zero-point energies. The value 1245.5 ±2.0 wave numbers is to be compared, therefore, with the value 1243.0 ±7.6 wave numbers deduced from the data of the present investigation, and indicates that, within the accuracy with which calorimetric measurements and spectroscopic analyses can be made today, the energies of atomic linkages are independent of the mass of the nuclei of the atoms.

VII. SUMMARY

The various thermodynamic values calculated in this paper are summarized in table 6.

TABLE 6.—*Summary of thermodynamic values*

Reaction	$\Delta H^\circ_{298.16}$		$\Delta F^\circ_{298.16}$		ΔH_0°	
	Int. j/mole	*cal*/mole*	*Int. j/mole*	*cal*/mole*	*Int. j/mole*	*cal*/mole*
$D_2(g)+1/2\ O_2(g)=D_2O(liq)$	$-294,663 \pm 94$	$-70,414.0 \pm 22.5$	$-243,470 \pm 100$	$-58,200.5 \pm 23.9$		
$D_2(g)+1/2\ O_2(g)=D_2O(g)$	$-249,172 \pm 100$	$-59,563.5 \pm 23.9$	$-234,521 \pm 100$	$-56,061.2 \pm 23.9$	$-246,231 \pm 100$	$-58,800.5 \pm 23.9$
$D_2O(liq)=D_2O(g)$	$45,391 \pm 36$	$10,850.5 \pm 8.6$	$8,949 \pm 9$	$2,139.2 \pm 2.2$		
$D_2(g)+H_2^1O(liq)=H_2^1(g)+D_2O(liq)$	$-8,770 \pm 83$	$-2,096.4 \pm 19.8$	$-6,316 \pm 96$	$1,509.8 \pm 22.9$		
$D_2(g)+H_2^1O(g)=H_2^1(g)+D_2O(g)$	$-7,386 \pm 90$	$-1,765.6 \pm 21.5$	$-5,966 \pm 90$	$1,426.1 \pm 21.5$	$-7,337 \pm 90$	$-1,753.9 \pm 21.5$

* The calorie is defined as 4.1833 int. j.

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RESEARCH PAPER RP1288

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NOTE ON THE EFFECT OF PRESSURE ON THE WAVELENGTHS OF THE INTERNATIONAL SECONDARY STANDARDS IN THE FIRST SPECTRUM OF IRON

By Curtis J. Humphreys

ABSTRACT

The wavelengths of the lines in the first spectrum of iron, adopted as secondary standards by the International Astronomical Union in 1928 and 1938, have been compared with the wavelengths of the same set of lines, observed by Burns and Walters using a vacuum-arc source. The International Standard wavelengths are derived from observations with the specified Pfund arc operated in air. Consequently the two sets of data permit a check on the pressure effect in Fe I. Term depressions obtained by this comparison agree reasonably well with those observed by Babcock.

The widespread use of the lines of the spectra of iron as standards of wavelength makes it important that the dependence of wavelengths upon operating conditions to which the source is subjected be determined. The Pfund arc, as specified by the International Astronomical Union [1],[1] is used as the source of the secondary standards in the iron spectra. The essential feature of the specification, that the radiation used be taken from the central zone of a relatively long arc, is intended to eliminate pole effect. The spectrum from this source is, however, subject to the displacement arising from the pressure of the atmosphere. The so-called vacuum arc, because of the relatively low operating pressure, exhibits a negligible pressure effect and the pole effect has not been detected in it.

Earlier investigations of the pressure effect, particularly in the spectra of iron, have been discussed by the author in a recent paper on the pressure effect in Fe II [2]. Reference is made here only to the work of Gale and Adams [3], and of Babcock [4]. Gale and Adams separated the observed lines into four groups, designated by the letters *a*, *b*, *c*, and *d*, according to the amount of pressure displacement. A fifth group, designated *e*, consisting of lines showing a negative pressure effect, that is a diminution of wavelength with increased pressure on

[1] Figures in brackets indicate the literature references at the end of this paper.

the source, was noted by St. John and Ware [5]. Group *e* is not considered in this study because it contains no secondary standards. It was shown by Babcock that this grouping could be explained on the basis of the term classifications of the lines, assuming that the effect of pressure manifests itself in a lowering of the spectral terms, being relatively greater for the higher terms. The results of Gale and Adams were considerably larger than Babcock's, a feature explained by the latter on the basis of the presence of both pole effect and pressure effect in the radiation. Babcock operated his source in air in accordance with the IAU specification for the production of standards free from pole effect. No further measurements of pressure displacements in Fe I have been reported during the past 11 years.

Additional information regarding the pressure effect in Fe I may be obtained from a study of available interference measurements. The International secondary standards [6] represent the mean of three or more concordant comparisons of the wavelengths from the Pfund arc with the primary standard or an equivalent group of noble-gas lines. Burns and Walters [7] have made interference measurements of the wavelengths of the lines of Fe I from the vacuum arc in like manner. Wavelengths of lines common to these two sets of data should show a systematic difference attributable to pressure effect.

It is the purpose of this note to report and discuss the depressions of the levels of Fe I, resulting from a pressure difference of 1 atmosphere, corresponding to the respective operating conditions of the Pfund arc, specified as the source of International secondary standard wavelengths, and the vacuum arc, used by Burns and Walters.

For purposes of this study, the lines were grouped according to multiplets. Burns and Walters give wave numbers computed from average terms in addition to the observed values for most lines. Both have been compared with the wave numbers appropriate to the International secondary standards. The computed wave numbers are dependent on the observations of several different lines and may therefore be regarded as somewhat more accurate than the individual observed wave numbers. Such computed wave numbers might also be expected to give a somewhat more regular set of pressure displacements when subtracted from the wave numbers belonging to the International lines. This expectation, however, was not uniformly supported by the results. Consequently, both sets of differences were given equal weight in deriving depressions of the terms resulting from pressure.

The calculation of the depressions of the terms of a spectrum from the pressure displacements of individual lines has been discussed by Babcock [4] and by the author [2]. These depressions are all relative to the lowest state, assumed to have zero depression, and can be computed to the extent permitted by the availibility of lines involving transitions between levels, one of which has a known depression. The results of this study are given in table 1.

TABLE 1.—*Term depressions in* Fe I

Term		Number of combinations	Depression resulting from 1 atmosphere pressure change		Term		Number of combinations	Depression resulting from 1 atmcsphere pressure change	
Designation	Magnitude		This analysis	Babcock	Designation	Magnitude		This analysis	Babcock
	cm^{-1}		cm^{-1}	cm^{-1}					
$a\ ^5D$	0		0. 000	0. 000	$x\ ^3D°$	45, 300	7	. 022	
$a\ ^5F$	7, 500		0. 000	0. 000	$y\ ^3G°$	45, 400	4	. 020	
$a\ ^3F$	12, 500		. 000	. 001	$x\ ^5G°$	45, 800	2	—. 015	
$a\ ^5P$	17, 700		. 003	. 003	16°	46, 720	2	. 025	
$a\ ^3P$	18, 700		. 004	. 002	17°	46, 745	1	. 030	
$a\ ^3H$	19, 600		. 004	. 003	18°	46, 888	2	. 030	
$z\ ^7D°$	19, 600	2	. 004	. 003	19°	46, 889	1	. 022	
$b\ ^3F$	20, 800		. 005	. 003	$y\ ^3P°$	46, 900	3	. 028	
$a\ ^3G$	22, 000		. 006	. 007	$z\ ^3H°$	47, 000	2	. 027	
$b\ ^3P$	22, 900		. 007		$w\ ^3D°$	47, 100	5	. 030	
$z\ ^7F°$	23, 000	3	. 008	. 006	21°	47, 177	1	. 030	
$b\ ^3G$	24, 100		. 008		23°	47, 419	1	. 037	
$z\ ^7P°$	24, 100	1	. 010	. 005	$z\ ^3S°$	47, 500	1	. 046	
1	24, 335		. 008		$b\ ^5F$	47, 700	2	. 037	. 033
2	24, 574		. 008		25°	47, 834	2	. 039	
3	24, 772		. 008		26°	47, 966	1	. 012	
$z\ ^5D°$	26, 200	21	. 009	. 008	28°	48, 163	1	. 012	
$z\ ^5F°$	27, 300	17	. 008	. 009	30°	48, 238	4	. 014	
$z\ ^5P°$	29, 400	5	. 014	. 012	31°	48, 289	1	. 022	
$z\ ^3D°$	31, 600	6	. 006	. 006	32°	48, 304	3	. 025	
$z\ ^3F°$	31, 700	6	. 015	. 008	36°	48, 702	1	. 021	
$y\ ^5D°$	33, 600	16	. 018	. 015	37°	49, 108	1	. 006	
$y\ ^5F°$	34, 200	20	. 010	. 013	40°	49, 242	1	. 016	
$z\ ^3P°$	34, 200	5	. 010	. 013	44°	49, 604	2	. 017	
$z\ ^5G°$	35, 400	16	. 009	. 011	45°	49, 627	1	. 021	
$z\ ^3G°$	35, 700	13	. 019	. 014	50	50, 342	1	. 023	
$y\ ^3F°$	37, 100	13	. 019	. 015	51	50, 377	2	. 028	
$y\ ^5P°$	37, 100	6	. 015	. 007	52	50, 423	3	. 034	
$y\ ^3D°$	38, 600	8	. 017	. 015	55	50, 534	2	. 038	
$x\ ^5D°$	40, 000	14	. 019	. 020	60	50, 808	1	. 033	
$x\ ^5F°$	40, 700	3	. 017		61	50, 833	2	. 028	
$z\ ^5S°$	40, 900	3	. 017	. 010	67	50, 998	1	. 019	
$y\ ^5G°$	43, 000	7	—. 008		70, 71	51, 148	1	. 042	
$a\ ^7D$	43, 400	5	. 036	. 027	72	51, 192	1	. 002	
$w\ ^5D°$	44, 000	3	. 011		73	51, 208	1	. 014	
7°	44, 243	1	. 014		75	51, 228	1	. 032	
9°	44, 415	1	. 041		$a\ ^3D$	51, 700	1	. 041	. 035
11°	44, 551	1	. 000		$c\ ^5D$	52, 000	1	. 036	. 029
$b\ ^5D$	45, 300	4	. 031	. 029					

The designations of the terms, or numbers assigned to unclassified levels, appearing in the first column are in the notation used by Bacher and Goudsmit [8]. Column 2 gives the relative term magnitudes starting with the ground state zero, as is customary in discussions of this spectrum. Entries rounded off to hundreds represent the average positions of the groups of multiple levels constituting known terms. This procedure follows Babcock's example in setting up the corresponding table. In column 3 the number of combinations with lower levels is indicated. Inasmuch as all lines were given equal weight, these numbers give an indication of the weight to be associated with the pressure displacement found for any term. No entries are shown

opposite the low and intermediate even terms. Displacements corresponding to these terms had to be adopted in a somewhat different manner, as explained below, so that the number of combinations of the low even terms with high odd terms does not have the same significance as that of the numbers entered. The fourth column contains the term depressions obtained by this comparison of the International standards with the Burns-Walters data; and finally, in the last column are the corresponding term depressions obtained by Babcock from his own observations.

While it is apparent that, in general, the term depression increases with elevation of the term, it is doubtful if the effect has been measured precisely enough to establish a definite functional relationship. The low $a\ ^5F$ term appears to have no displacement relative to the ground state $a\ ^5D$, as shown by lines involving combinations with higher common odd levels. On the same basis the moderately low $a\ ^3F$ and $a\ ^5P$ do not show a displacement relative to $a\ ^5D$. The low odd septets are only slightly higher than $a\ ^5P$, and exhibit a measurable pressure displacement, which is apparent in the relatively intense intersystem combinations with the ground state. Even levels of the same magnitude are expected to show about the same pressure displacements. This would lead to the expectation that the even levels between 19,000 and 24,000 cm^{-1} would be displaced relative to the low terms. Combinations with high odd terms indicate that these levels have about the same displacement as $a\ ^5P$ but about 0.007 cm^{-1} greater on the average than $a\ ^3F$. Inasmuch as other evidence shows $a\ ^3F$ and $a\ ^5P$ to be affected about the same by pressure, it is seen that the results are somewhat contradictory. The values assigned to the even levels between 17,500 and 24,000 appear to be the best possible compromise, but are to a certain extent arbitrary.

The term depressions which can be compared with Babcock's show reasonably satisfactory agreement, so that his conclusions regarding the relationship between pressure displacement and term magnitude are supported by most of the results here presented. No clear-cut evidence for a systematic difference between the displacements of triplets and terms of higher multiplicities is shown. There is, therefore, no separate listing in the table. Babcock's observations were limited to the wavelength interval 3895 to 6677 A. The International standards, including those adopted at the most recent meeting of the IAU [6], cover the interval 2447 to 6677 A.

The pressure displacements obtained from data in the interval between 2447 and 3895 A frequently come out unexpectedly small and occasionally exhibit negative values. Inclusion in this paper of data from the region of wavelengths shorter than 3895 A has the effect of making many of the observed term depressions smaller than expected on the basis of earlier estimates. Whether there is any theoretical significance to be attached to this fact, it is impossible to say at present. However, attention should be called to the diminishing precision of observations as one goes toward the ultraviolet. Two reasons for this may be mentioned. The first is inherent in the Fabry-Perot interferometer and arises from a falling off of the reflecting power of metal films with diminishing wavelengths, resulting in poorer definition of interference fringes. The second reason is that the ratio $d\lambda/d\mu$ decreases toward the ultraviolet. In a determination

of term depressions, one is at a disadvantage because line displacements are measured, whereas it is a change in wave number which is required.

Because of the need of improved standards in the ultraviolet region and of the desirability of obtaining better agreement with the pressure displacements observed in the visible region, it is apparent that additional precise observations could be profitably undertaken.

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SEPARATION OF THE AROMATIC HYDROCARBONS, AND THE ISOLATION OF *n*-DODECANE, NAPHTHALENE, 1-METHYLNAPHTHALENE, AND 2-METHYLNAPHTHALENE, FROM THE KEROSENE FRACTION OF PETROLEUM[1]*

By Beveridge J. Mair and Anton J. Streiff[2]

ABSTRACT

This paper is the first report on the separation of the hydrocarbons in the kerosene fraction of petroleum, which investigation is being carried on as part of the work of the American Petroleum Institute Research Project 6. That part of the petroleum distilling between 114° and 144° C at a pressure of 56 mm Hg (corresponding approximately to 200° and 230° C at 760 mm Hg) was separated into a series of substantially constant-boiling fractions. From the material distilling between 127° and 133° C (at 56 mm Hg), *n*-dodecane was isolated by crystallization. All of the material except the isolated *n*-dodecane was then subjected to a systematic extraction with reflux in a two-solvent process in order to separate the aromatic hydrocarbons from the paraffins and naphthenes. The "clean-up" of the traces of aromatic hydrocarbons was accomplished by adsorption with silica gel. The aromatic fractions were then systematically distilled in fractionating columns of high efficiency. From the material boiling at 56 mm Hg between 127.0° and 127.5° C, 145° and 146.5° C, and 148.5° to 149.0° C, respectively, naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene were isolated by fractional crystallization.

"Best" lots of each of the four hydrocarbons were prepared, with impurities estimated to be, in terms of mole fraction: *n*-dodecane, 0.0000 ±0.0006; naphthalene, 0.0006 ±0.0004; 1-methylnaphthalene, 0.0025 ±0.0011; 2-methylnaphthalene, 0.0000 ±0.0003. Values of certain physical properties of these four hydrocarbons, all extrapolated to material of 100 percent were determined as follows:

Hydrocarbon	*n*-Dodecane	Naphthalene	1-Methylnaphthalene	2-Methylnaphthalene
Boiling point at 760 mm Hg...°C	216.26 ±0.03	217.96 ±0.03	244.78 ±0.10	241.14 ±0.05
Freezing point in air.....°C	−9.60 ±0.02	80.27 ±0.02	−30.77 ±0.06	34.44 ±0.02
Density at $t°$ C.....g/ml	0.74512 ±0.00005	0.9752 ±0.0002	1.0163 ±0.0001	0.99045 ±0.00005
Refractive index at $t°$ C.....n_D	1.41951 ±0.00010	1.5898 ±0.0002	1.61494 ±0.00010	1.60192 ±0.00010
Refractive dispersion at $t°$ C n_F-n_C	0.00733 ±0.00010	0.0289 ±0.0002	0.02995 ±0.00010	0.02899 ±0.00010
Temperature of density, refractive-index, and dispersion measurements.....°C	25	85	25	40

[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

[2] Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

* Presented at the meeting of the Division of Petroleum Chemistry, American Chemical Society, in Cincinnati, Ohio, April 8–12, 1940.

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I. INTRODUCTION

The work on the chemical constitution of petroleum being carried on at this Bureau by the American Petroleum Institute Research Project 6 was extended in July 1938 to the kerosene fraction. This paper constitutes the first report of this work on the kerosene fraction and describes the separation of the aromatic hydrocarbons from the paraffins and naphthenes and the isolation of *n*-dodecane, naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene.

II. ORIGIN OF THE KEROSENE STOCK AND OUTLINE OF THE INVESTIGATION

The kerosene stock came from the lot (approximately 1,000 gallons) of crude petroleum already used in the investigation of the gasoline and lubricant fractions of petroleum by the American Petroleum Institute Research Project 6 [1].[3] This material was obtained in 1928 from the Brett No. 6 well in the Ponca City Field in Oklahoma. The crude petroleum was first separated in a semicommercial plant by the Sun Oil Co. into quantities which could be handled in the laboratory. The treatment of the kerosene fraction, after receipt at the laboratory, is shown schematically in figure 1. The first stage was a systematic distillation at a pressure of 56 mm Hg of all fractions which contained any material boiling in the range desired for this investigation, 114° to 144° C at 56 mm Hg (approximately 200° to 230° C at 760 mm Hg). The greater part of the *n*-dodecane was then removed by crystallization from the fractions which distilled between 127° and 133° C. The remainder of the distillation fractions and the mother liquors from the crystallization of the dodecane were separated by extraction with methyl cyanide and Marcol into two portions: (1) fractions of aromatic hydrocarbons and (2) raffinate fractions containing paraffins and naphthenes with about 2½ percent of aromatics. The aromatic hydrocarbons were removed

[3] The numbers in brackets indicate the literature references at the end of this paper.

from the second portion by adsorption with silica gel, and the adsorbed portion was reextracted with the two solvents. The original petroleum distillate was thus separated into a series of fractions containing aromatic hydrocarbons and a series containing paraffins and naphthenes. The aromatic fractions were then systematically distilled in columns of high efficiency, and from the aromatic material boiling at 56 mm Hg in the ranges 127° to 127.5° C, 145° to 146.5° C, and 148.5° to 149.0° C, respectively, naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene were isolated.

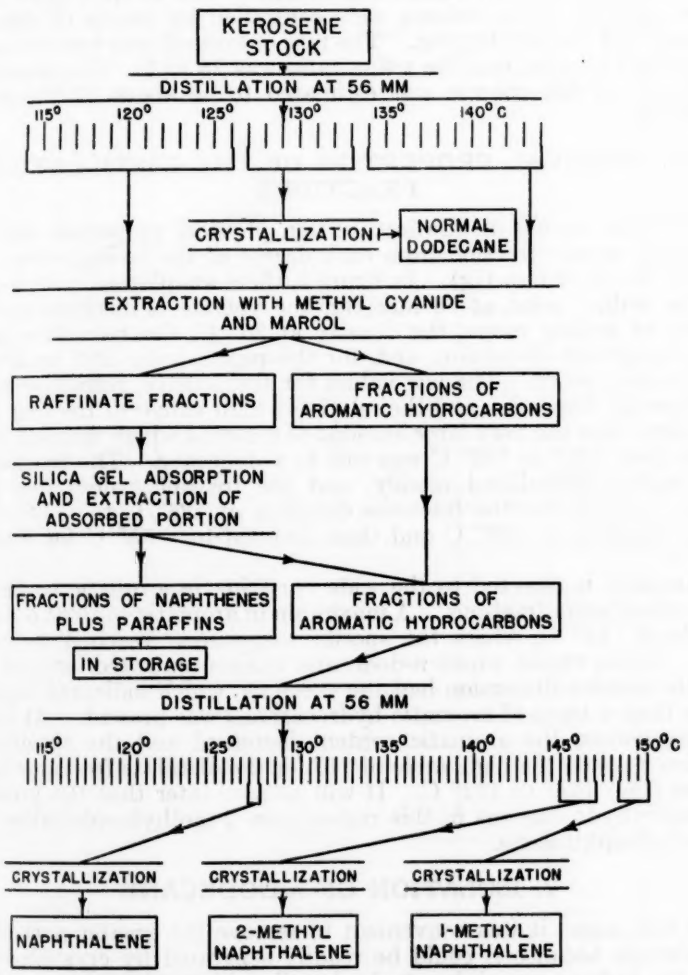

FIGURE 1.—*Schematic outline of the investigation.*

III. SYSTEMATIC DISTILLATION OF THE ORIGINAL DISTILLATE

The kerosene stock referred to in the preceding paragraph was systematically distilled twice at 56 mm Hg in a still which consisted of a 12-liter spherical Pyrex glass pot sealed to a Pyrex glass column 5 cm in diameter and 250 cm in length. This column was fitted with the type of reflux regulator recently described by Rossini and Glasgow [2] and was packed with single-turn helices (0.24 cm in diameter) made of No. 30 AWG stainless-steel wire. The temperatures of the three sections of the column were controlled by means of electrical heating and thermal lagging. The rate of take-off was approximately 1.5 ml per minute, and the reflux ratio was 25 to 1. The separating efficiency of this column was estimated to be about 50 theoretical plates [3].

IV. PHYSICAL PROPERTIES OF THE DISTILLATION FRACTIONS

After the second distillation, certain physical properties were determined on one fraction from each degree of the boiling range 114° to 144° C (at 56 mm Hg). In figure 2, there are plotted, with respect to the boiling point at 56 mm Hg, the volume of distillate for each degree of boiling range, the density at 25° C, the refractive index, n_D^{25}, the specific dispersion, and, for the region from 126° to 134° C, the freezing point. The low values for the density, refractive index, and specific dispersion and the relatively high values of freezing point indicated that the very large amount of material which distilled in the range from 128° to 132° C was rich in *n*-dodecane. The fractions in this region crystallized readily, and the freezing points rose from about −60° C for the fractions distilling at 126° C to −14° C for those distilling at 130° C and then dropped to −55° C for those at 133° C.

Attention is directed to the wide variation in aromatic content of these distillation fractions. A maximum in aromatic content occurred at about 119° C, where the specific dispersion [4] reached the value 129. In the region where *n*-dodecane was concentrated (around 130° C), the specific dispersion had the value 99, which indicated that not more than a trace of aromatic hydrocarbons was present. At higher boiling points, the aromatic content increased and the specific dispersion reached the high value of 140 for the distillate fractions in the region from 141° to 142° C. It will be seen later that the principal aromatic hydrocarbons in this region were 2-methylnaphthalene and 1-methylnaphthalene.

V. ISOLATION OF *n*-DODECANE

At this stage, it was convenient to remove the greater part of the *n*-dodecane because it could be readily separated by crystallization, and the volume remaining to be handled in the later more tedious processes would thus be substantially reduced. Also the presence of the *n*-dodecane would complicate the extraction process to be used later.

The *n*-dodecane was removed from the fractions distilling between 127° and 133° C (at 56 mm Hg) by fractional crystallization with the

[4] Unless otherwise specified, the specific dispersion is expressed in units of $10^4 \times (n_f - n_c)/d$.

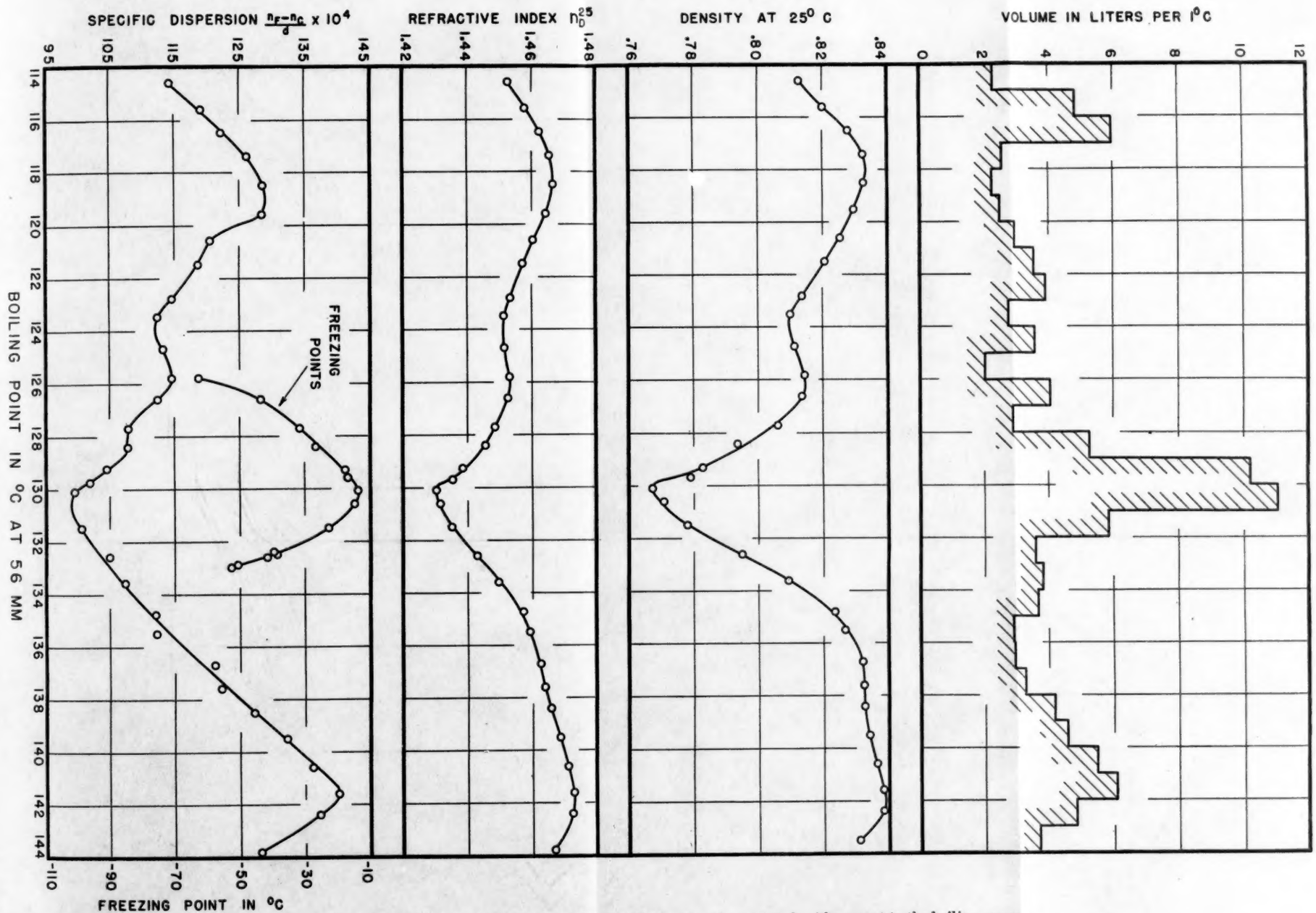
SPECIFIC DISPERSION $\frac{n_F - n_C}{\rho}$ x 10^4
REFRACTIVE INDEX n_D^{25}
DENSITY AT 25° C
VOLUME IN LITERS PER 1°C
BOILING POINT IN °C AT 56 MM
FREEZING POINTS
FREEZING POINT IN °C

FIGURE 2.—*Properties and volume of the distillation fractions plotted with respect to the boiling range.*

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FREEZING POINT IN °C

low-temperature centrifuge described by Hicks-Bruun and Bruun [4]. The procedure used was to mix fractions with similar freezing points (determined approximately with a toluene-in-glass thermometer) and to repeat the crystallizations until the material was entirely separated into substantially pure *n*-dodecane and material so poor in dodecane that it yielded not more than a trace of crystals on cooling to −65° C. Certain physical properties, the volume, and the purity of the fractions of *n*-dodecane obtained by this process are recorded in table 1. The percentage of the total distillate, 114° to 144° C (at 56 mm Hg), constituted by the volume of *n*-dodecane isolated is recorded in table 9.

TABLE 1.—*Volume and properties of the various lots of crude n-dodecane actually isolated*

Lot	Volume	Refractive index at 25° C	Freezing point in air	Amount of impurity [a]
	ml	n_D	*°C*	*Mole fraction*
1	3,340	1.4199	−9.83	0.014 ±0.003
2	3,740	1.4200	−9.88	.018 ±0.004
3	3,240	1.4204	−10.09	.030 ±0.006
4	2,360	1.4206	−10.22	.038 ±0.008
5	2,230	1.4224	−11.28	.100 ±0.020
Total	14,910			

[a] Amount of liquid-soluble, solid-insoluble impurity, calculated from the lowering of the freezing point, and using for the freezing point of pure *n*-dodecane the value −9.60 (see table 2) and for the heat of fusion the value 8,730 cal/mole [5]. The freezing point of a given lot was taken to be the highest temperature observed with crystals present. This temperature was attained at from 3 to 6 minutes from the start of supercooling. This would corespond to about 4 to 8 percent of the material frozen.

To obtain a pure sample of *n*-dodecane, some of lot 1, described in table 1, was diluted with an equal volume of diethyl ether, and was crystallized and centrifuged. The crystal portion was again dissolved in an equal volume of ether, crystallized, and centrifuged. The solvent was removed by refluxing at 56 mm Hg. The time-temperature cooling curve for this best lot of *n*-dodecane is shown in figure 3. On the basis of this curve, the amount of impurity in this best lot was estimated [6] to be 0.0000 ±0.0006 mole fraction.

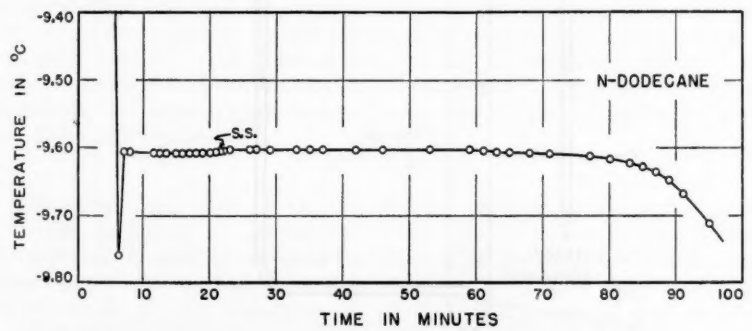

FIGURE 3.—*Time-temperature cooling curve for n-dodecane.*

SS denotes the time at which the stirrer stopped. The scale of ordinates gives the temperature in °C. The scale of abscissas gives the time in minutes.

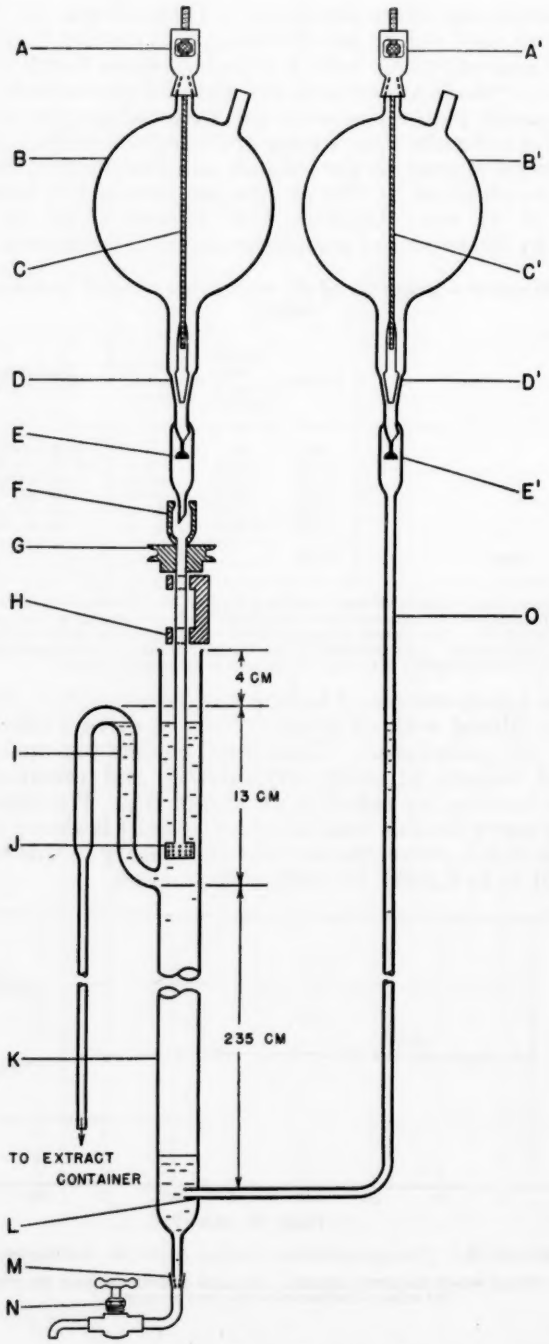

FIGURE 4.—*Extraction apparatus.*

The properties of the best *n*-dodecane from this petroleum are given in table 2, together with values previously determined for this substance by Shepard, Henne, and Midgley [7] and by Mair [8].

TABLE 2.—*Properties of n-dodecane*

Material	From petroleum, Mair and Streiff		Shepard, Henne, and Midgley [7]	Mair [8]
	(*A*) Actual "best" lot[a]	(*B*) Extrapolated to a purity of 100 percent		
Boiling point at 760 mm, °C	[b]216.26 ±0.03	216.26 ±0.03	216.23	
Boiling point at 57.78 mm, °C	[b]131.33 ±0.05	131.33 ± .05		
Freezing point in air, °C	−9.60 ±0.01	−9.60 ±0.02	−9.73	−9.61
Density at 20°C, g/ml	[c](0.7486) ±0.0001	(0.7486) ±0.0001		
Density at 25°C, g/ml	[d].74512 ±0.00002	.74512 ±0.00005	0.74542	
Refractive index at 20°C, n_D	[c](1.4217) ±0.0001	(1.4217) ±0.0001	1.42188	
Refractive index at 25°C, n_C	[e]1.41736 ±0.00010	1.41736 ±0.00010	1.41752	
Refractive index at 25°C, n_D	[e]1.41951 ±0.00010	1.41951 ±0.00010	1.41967	1.41952
Refractive index at 25°C, n_F	[e]1.42469 ±0.00010	1.42469 ±0.00010	1.42501	
Refractive dispersion at 25°C, n_F-n_C	0.00733 ±0.00010	0.00733 ±0.00010	0.00749	
Specific dispersion at 25°C, $(n_F-n_C)/d$	0.00984 ±0.00010	0.00984 ±0.00010	0.0100	

[a] Amount of impurity estimated to be 0.0000 ±0.0006 mole fraction.
[b] Determined by C. B. Willingham and F. D. Rossini.
[c] These values were estimated from the values observed at 25° C.
[d] Determined by the Capacity and Density Section of this Bureau.
[e] Determined by L. W. Tilton of the Optical Instruments Section, of this Bureau.

VI. PROCESS OF EXTRACTION

1. METHOD

The next step in the separation of the kerosene stock was to subject it to an efficient process of extraction with solvents to separate the aromatic hydrocarbons from the paraffins and naphthenes. There was used for this purpose a system of two solvents, methyl cyanide [5] and Marcol, which is a commercial aromatic-free mixture of paraffins and naphthenes having an initial boiling point of about 230° C at 56 mm Hg. The methyl cyanide served to separate the kerosene stock into a "raffinate" portion, which consisted of a mixture of paraffins and naphthenes with about 2½ percent of aromatic hydrocarbons, and an "extract" portion, which consisted mainly of aromatic hydrocarbons but had an appreciable amount of paraffins and naphthenes. The "extract" portion, including the solvent, methyl cyanide, was then treated with Marcol to produce an aromatic portion substantially free from paraffins and naphthenes and an unresolved portion containing all three types of hydrocarbons. The unresolved portion was then reprocessed.

2. APPARATUS

The apparatus used in the extraction process is shown diagrammatically in figure 4. Referring to this figure, kerosene is contained in reservoir *B* and is allowed to flow at a controlled rate through glass valve *D* to the top of rotating shaft *F*. It then flows down the hollow shaft to the enlargement in the distributor *J* and is there

[5] For this material, methyl cyanide appears to have about the same selectivity for aromatic hydrocarbons as does sulfur dioxide. Furthermore, the methyl cyanide can be used at room temperature in apparatus not closed to the atmosphere. The methyl cyanide used was purified by distillation.

forced through small holes and dispersed in the form of small globules in the solvent contained in the column, K.[6] These globules fall to the bottom of the column and form a layer which is withdrawn intermittently through the valve, N. The solvent is contained in reservoir B' and is admitted at a controlled rate through glass valve D', and tube O to the bottom of the column. The extract portion flows through tube I (where small globules of oil have an opportunity to settle out and return to the column) to a collecting bottle.

Some details of the extractor may be added. The rate of flow of kerosene or solvent was adjusted by means of screws AA' attached through tungsten rods CC' to the solid ground glass stoppers which fit in sockets DD'. These devices have been described by Rossini and Glasgow [2], and a detailed drawing of them is given in figure 4 of their paper. The rate of flow may be computed from the number of drops leaving glass hemispheres EE'. The distributor, rotating in bearing H, was operated at a speed of 500 rpm. The enlargement in distributor J contains 30 holes in each of the three rows, each hole being 0.035 cm in diameter. Valve N is a small brass needle valve which is attached to the bottom of the column through copper tubing and through the ground and tapered brass-to-glass joint M. This joint is tightly sealed with soft solder [9]. The reservoirs are of 1-liter capacity. The diameter of the column is 3 cm. Other dimensions of the column may be obtained from figure 4.

3. PROCEDURE

The extraction procedure is illustrated schematically in figure 5. Extractors 1 and 2 were operated in series. In extractor 1 partially extracted kerosene from extractor 2 was reextracted with fresh methyl cyanide and yielded kerosene raffinate fractions with values for the specific dispersion of about 100, which indicated the presence of about 2.5 percent of aromatic hydrocarbons. The methyl cyanide extract from extractor 1 was used as solvent in extractor 2 with the original kerosene. In extractor 3 the methyl cyanide extract was reextracted with Marcol and yielded a methyl cyanide extract substantially free from naphthenes and paraffins. The Marcol, however, dissolved some aromatic hydrocarbons in addition to the naphthene and paraffin hydrocarbons, so that it was necessary to separate these kerosene hydrocarbons from the Marcol by distillation and recycle them as shown in figure 5.

The rate of flow of methyl cyanide was from 3 to 4 ml per minute; of kerosene from 0.6 to 0.9 ml per minute; and of Marcol about 0.4 ml per minute. Beginning at the low end of the boiling range, charges of kerosene distillation fractions covering a range of 1° C (except for the dodecane mother liquors which covered a 6° C range)

[6] In preliminary experiments, kerosene was allowed to flow through an auxiliary tube into an open rotating basket. We are indebted to C. B. Willingham for suggesting the use of a hollow shaft.

were fed successively to the extractors. The extract and raffinate fractions were collected according to the boiling range of the charge from which they came, although, owing to the "hold-up" of the columns, a precise demarcation of material from successive charges was not possible.

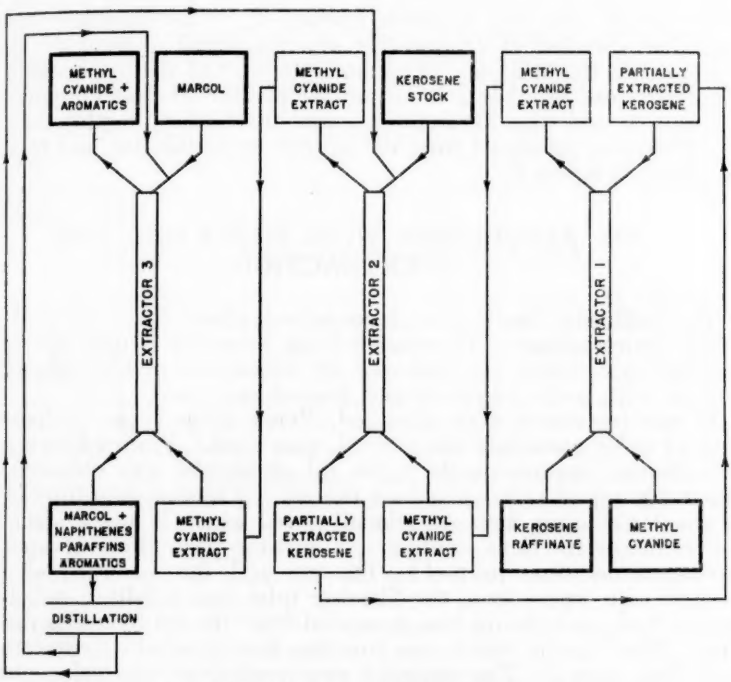

FIGURE 5.—*Schematic diagram of the extraction process.*

It will be seen that as a result of this process there were obtained from the extractors the following three fractions:

1. A raffinate portion from extractor 1 which contained naphthenes and paraffins with about 2.5 percent of aromatic hydrocarbons and a small quantity of methyl cyanide.

2. An extract portion from extractor 3 which contained the greater part of the methyl cyanide and the aromatic hydrocarbons, with substantially no naphthenes or paraffins. In addition, this portion contained a small quantity of Marcol.

3. An unresolved portion which contained the Marcol and the naphthenes and paraffins and aromatics from extractor 3. This portion contained also a small amount of methyl cyanide.

Three stills with rectifying sections 90 cm long packed with stainless steel helices were used in the further treatment of these fractions. Fraction 1 (the raffinate portion) was refluxed in one of these stills at 56 mm Hg and the small amount of methyl cyanide which it contained was caught in a trap maintained at the temperature of solid carbon dioxide. After cooling the fraction, it was siphoned from the still pot. The greater part of the methyl cyanide was removed from fraction 2 by distillation at atmospheric pressure and the last traces at 56 mm Hg, as with fraction 1. The aromatic material was then distilled at 56 mm Hg and the small amount of Marcol remained in the still pot. The small amount of methyl cyanide was removed from fraction 3 in a manner similar to that employed for fraction 1 and the kerosene portion (aromatics, naphthenes and paraffins) was separated from the Marcol by distillation and recycled, as shown in figure 5.

VII. ADSORPTION WITH SILICA GEL AND REEXTRACTION

The raffinate fractions still contained about 2½ percent of aromatic hydrocarbons. To remove these aromatic hydrocarbons, adsorption with silica gel, followed by extraction of the gel-retained portion with methyl cyanide and Marcol, was used.

In the treatment with silica gel, Pyrex tubes 4 cm in diameter, each of which contained 500 g of gel, were used. From 2-liter charges of raffinate, approximately 1,700 ml of filtrate was obtained and about 300 ml of oil remained on the gel. (Greater quantities of gel, or smaller charges, were occasionally used where it was evident that the raffinate fractions contained a greater percentage of aromatic hydrocarbons than normal.) The gel and the adsorbed oil were flushed with water from the filtering tube into a 5-liter, round-bottomed flask, and the oil was separated from the gel by steam distillation. The filtrate, which was now free from aromatic hydrocarbons, was then stored. The material recovered from the gel contained about 20 percent of aromatic hydrocarbons, and was separated as before, by extraction with methyl cyanide and Marcol, into a raffinate portion and a portion consisting substantially of aromatic hydrocarbons. This raffinate, of much smaller volume than the original, was further separated by adsorption into a filtrate and an adsorbed portion, and the adsorbed portion again separated by extraction into a raffinate and an aromatic portion. This process was repeated until all the oil was resolved into filtrate fractions consisting of naphthenes plus paraffins and extract fractions consisting substantially of aromatic hydrocarbons.

In the first filtration of raffinate through silica gel, a sufficient quantity of material was available to prepare charges and store filtrate fractions with distillation ranges of only one or two degrees. However, in the subsequent resolution of the adsorbed material into fractions consisting of naphthenes plus paraffins and fractions con-

sisting of aromatic hydrocarbons, the material was treated in two ranges: one distilling from 114° to 134° C, the other from 134° to 144° C.

VIII. SYSTEMATIC DISTILLATION OF THE AROMATIC MATERIAL

The aromatic material obtained from the process of extraction with solvents was systematically distilled at a pressure of 56 mm Hg in a column which had a rectifying section 2.5 by 280 cm and a separating efficiency corresponding to about 100 theoretical plates [10]. The reflux ratio was about 30 to 1, and the distillate was removed at the rate of about 0.2 ml per minute and collected in fractions of 50 ml.

Figure 6 gives the distribution of the aromatic material by volume with respect to the boiling point at a pressure of 56 mm Hg. Of the several pronounced peaks which may be observed in the volume curve in figure 6, attention is particularly directed to those occurring at 127.0° to 127.5° C, 145.0° to 146.5° C, and 148.5° to 149.0° C, from which material naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene, respectively, were isolated later.

IX. ISOLATION OF NAPHTHALENE

During the distillation of the aromatic material which was separated from the original petroleum distillate boiling at 118° to 120° C, crystals formed in the condenser of the distilling column and in the tubes leading to the receiver. The boiling point of this material was near that to be expected for naphthalene at 56 mm Hg; namely, about 127° C. The undistilled residue from this charge had a volume of about 400 ml, it crystallized to a solid mass at room temperature, and obviously was rich in naphthalene. Additional residues of 144 and 100 ml of substantially the same material were obtained from the distillation of the aromatic material separated from the original petroleum distillate boiling at 120° to 121° C, and at 121° and 123° C. These residues, rich in naphthalene, are represented by the shaded block at the temperature 127.0° to 127.5° C in figure 6.

It is apparent that the bulk of the naphthalene is found in those fractions of the original petroleum distillate which, at 56 mm Hg, distil at about 120° C, that is, 7° C below the boiling point of pure naphthalene at this pressure. For the alkylbenzenes occurring in this region, no marked displacement of boiling point was observed, though a small displacement of one or two degrees may exist. This difference in behavior of alkylbenzenes and naphthalene helps to explain the highly concentrated naphthalene residues which were obtained by distillation alone. That is, the aromatic material separated from the original petroleum distillate boiling at 118° to 120° C contained alkylbenzenes boiling at about 119° to 122° C and naphthalene boiling at 127° C. The naphthalene may readily be separated by distillation from the mononuclear aromatics associated with it. As shown in figure 6, the additional aromatic material which was found to distil in the neighborhood of 127° C came principally from kerosene which distilled at or slightly above this temperature, and its refractive index, n_D^{25}=1.50 to 1.51, indicated that this was substantially mononuclear aromatic material.

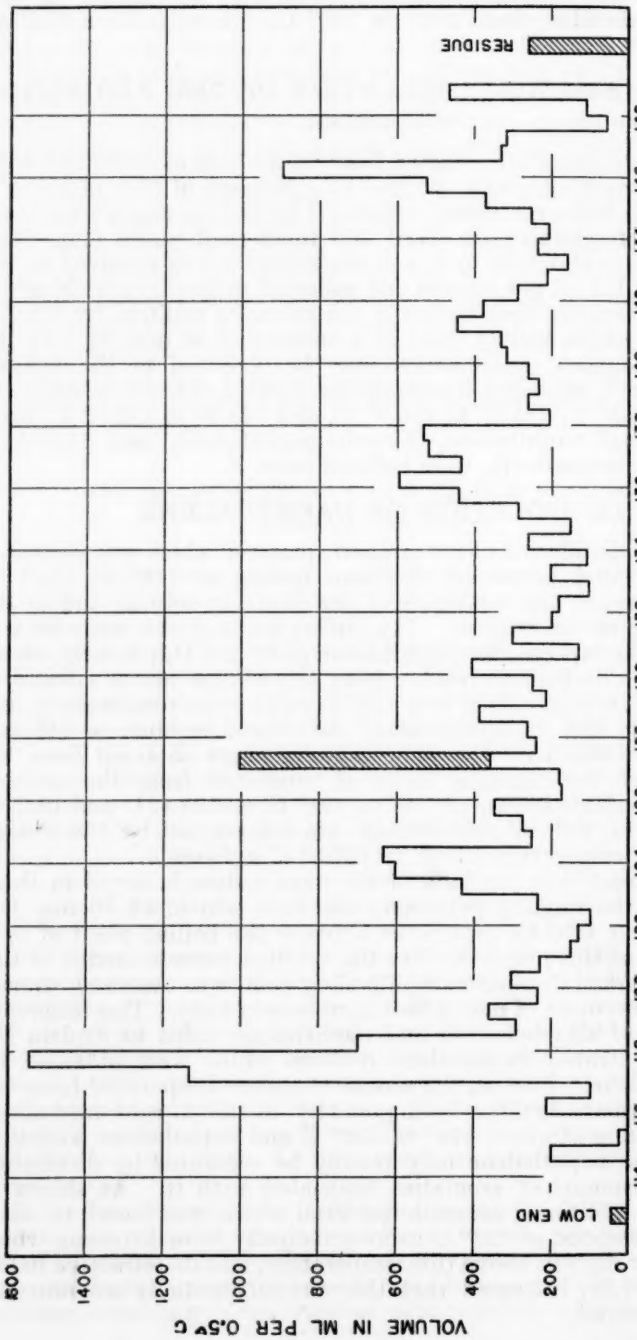

FIGURE 6.—*Distribution of the aromatic distillate by volume with respect to the boiling point.*

The scale of ordinates gives the volume in ml for each 0.5° C fraction. The scale of abscissas gives the boiling point of these fractions in °C at a pressure of 56 mm Hg.

The naphthalene was purified by systematic crystallization from ethyl alcohol. The residues rich in naphthalene were dissolved in a minimum of hot alcohol, the solution was cooled to about 10° C, and the crystals were removed by filtration with suction. Second crops of crystals were obtained by distilling off a portion of the alcohol in a fractionating column and again cooling and filtering with suction. The original naphthalene residues from the still pot were highly colored, and this color was used as a basis for blending fractions and for following the process of purification. Oil was recovered from the final alcoholic solution of mother liquors by distilling off the greater part of the alcohol, then diluting the solution with water and separating the oil phase. Before determining the freezing point, the naphthalene was first distilled at 56 mm Hg to remove all traces of solvent. The volumes, percentages of impurities, and certain physical properties of the various lots of crude naphthalene are recorded in table 3. As is evident from the low refractive index, the recovered oil contained little

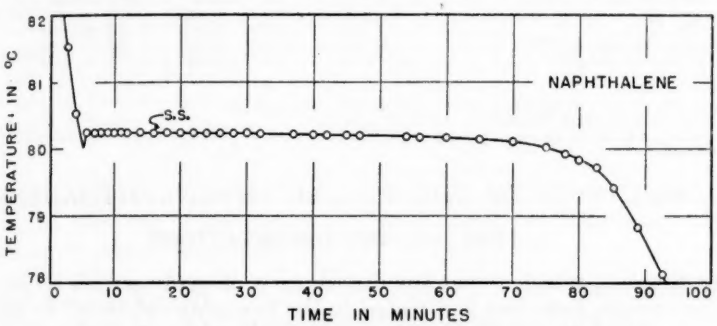

FIGURE 7.—*Time-temperature cooling curve for naphthalene.*

SS denotes the time at which the stirrer stopped. The scale of ordinates gives the temperature in °C. The scale of abscissas gives the time in minutes.

naphthalene. The percentage of the total distillate, 114° to 144° C at 56 mm Hg, constituted by the volume of naphthalene actually isolated, is recorded in table 9.

TABLE 3.—*Volumes and properties of the various lots of crude naphthalene actually isolated*

Lot	Volume	Refractive index at		Freezing point in air	Amount of impurity [a]
		85° C	25° C		
	ml	n_D	n_D	°C	*Mole fraction*
1. Crystals I	395	1.5898		80.24	0.0006 ±0.0004
2. Crystals II	40	1.5749		72.0	.12 ±0.02
3. Oil	132		1.5383		

[a] Amount of liquid-soluble, solid-insoluble impurity, calculated from the lowering of the freezing point, using 80.27° C (see table 4) for the freezing point of pure naphthalene and 4,610 cal/mole as its heat of fusion [5]. The freezing point of a given lot was taken to be the highest temperature observed with crystals present. This temperature was attained for lot 1 about 1 minute from the start of supercooling. This would correspond to about 1.5 percent of the material frozen.

The time-temperature cooling curve of the best lot of naphthalene (lot 1 in table 3) is shown in figure 7, which gives an initial freezing point of 80.24° C. On the basis of this curve, the amount of impurity in this best lot of naphthalene was estimated [6] to be 0.0006 ± 0.0004

mole fraction, and the freezing point of pure naphthalene was estimated to be 80.27° C. A recrystallization of this best lot from alcohol, followed by a distillation at 56 mm Hg, failed to improve the purity, the freezing point of the material being unchanged within the experimental error (actually lower by 0.003° C).

The properties of the best naphthalene from petroleum are given in table 4, together with values of other investigators.

TABLE 4.—*Properties of naphthalene*

Material	From petroleum, Mair and Streiff		Auwers and Frühling [11]
	(*A*) Actual "best" lot [a]	(*B*) Extrapolated to a purity of 100 percent	
Boiling point at 760 mm °C	[b]217.96 ±0.03	217.96 ±0.03	
Boiling point at 57.78 mm °C	[b]128.51 ±0.10	128.51 ±0.10	
Freezing point in air °C	80.24 ±0.01	80.27 ±0.02	
Density at 85° C g/ml	0.9752 ±0.0002	0.9752 ±0.0002	[c](0.9751
Refractive index at 85° C n_D	1.5898 ±0.0002	1.5898 ±0.0002	[c](1.5900
Refractive dispersion at 85° C $n_F - n_C$	0.0289 ±0.0002	0.0289 ±0.0002	
Specific dispersion at 85° C $(n_F - n_C)/d$	0.0297 ±0.0002	0.0297 ±0.0002	(0.0298)

[a] Amount of impurity estimated to be 0.0006 ±0.0004 mole fraction.
[b] Determined by C. B. Willingham and F. D. Rossini.
[c] Computed from the values 0.9641 and 1.5827 observed at 99.6° C for the density and refractive index, respectively.

X. ISOLATION OF THE TWO METHYLNAPHTHALENES

1. PRELIMINARY OBSERVATIONS

In figure 6, which shows the distribution of volume with respect to boiling range, attention is directed to the two peaks at 145.0° to 146.5° C and 148.5° to 149.0° C. A considerable number of the distillate fractions in the region from 145.0° to 146.5° C were solid at room temperature, and a few, boiling at 146.4° C, had freezing points of 31° to 32° C and refractive indices, $n_D^{40}=1.601$. Judging from these properties, this material was principally 2-methylnaphthalene. As the boiling point of the fractions increased from 146.4° to 148.3° C, the freezing point decreased to −47° C; then as the boiling point increased from 148.3° to 148.9° C, the freezing point increased, and a distillate fraction with freezing point equal to −31.9° C and $n_D^{25}=1.6142$ was obtained. This fraction was obviously rich in 1-methylnaphthalene.

As with naphthalene, the 1- and 2-methylnaphthalenes were obtained from fractions of the original petroleum distillate boiling approximately 6° or 7° C below the boiling points of the respective methylnaphthalenes. The boiling point ranges of the material from which these two hydrocarbons were obtained overlapped, and it was principally from charges of aromatic material extracted from the original kerosene boiling in the range 139° to 140° C that aromatic distillate fractions solid at room temperature and very concentrated in 2-methylnaphthalene were obtained. Charges of aromatic material extracted from the original kerosene boiling at 141° to 144° C yielded some fractions which distilled at about 146.5° C, and contained, in addition to 2-methylnaphthalene, a considerable amount of 1-methylnaphthalene. These fractions were not solid at room temperature. Higher-boiling fractions from these same charges were of course richer

in 1-methylnaphthalene. Before proceeding with the isolation of these compounds by fractional crystallization, some of the material was concentrated further by a second distillation. All fractions which distilled from 142° to 146° C and had freezing points below 22° C were combined for one distillation. An additional volume of material rich in 2-methylnaphthalene was thus obtained. The residue from this distillation, together with all fractions which distilled from 146° to 148.5° C and which had freezing points below 22° C, were combined for a second distillation. This second distillation yielded fractions in the region from 146° to 146.5° C which were rich in 2-methylnaphthalene, and fractions in the region from 148.5° to 149.0° C with freezing points which indicated they were on the 1-methylnaphthalene side of the eutectic of 2-methylnaphthalene and 1-methylnaphthalene.

2. ISOLATION OF 2-METHYLNAPHTHALENE

The 2-methylnaphthalene was isolated by systematic crystallization, using an equal volume of ethyl alcohol as solvent and centrifuging the crystals. The freezing point of the fractions served as a basis for mixing various fractions for crystallization and for following the process of purification. The fractions were refluxed at 56 mm Hg to remove solvent before determining their physical properties. The volumes, certain physical properties, and the amounts of impurities of the various lots of crude 2-methylnaphthalene actually isolated are shown in table 5. The percentage of the total distillate, 114° to 144° C at 56 mm Hg, constituted by the 2-methylnaphthalene actually isolated, is recorded in table 9.

TABLE 5.—*Volumes and properties of the various lots of 2-methylnaphthalene actually isolated*

Lot	Volume	Refractive index at 40° C	Freezing point in air	Amount of impurity [a]
	ml	n_D	*°C*	*Mole fraction*
1. Crystal I	962	1.6015	33.81	0.009±0.002
2. Crystal II	470	1.5988	31.25	.023±0.005
3. Mother liquors	535	1.5566	−24	----------

[a] Amount of liquid-soluble, solid-insoluble impurity, calculated from the lowering of the freezing point, using 34.44° C (see table 6) for the freezing point of pure 2-methylnaphthalene and 2,850 cal/mole as its heat of fusion [5]. The freezing point of a given lot was taken to be the highest temperature observed with crystals present. This temperature was attained at about 5 minutes from the start of supercooling. This would correspond to about 7 percent of the material frozen.

To obtain a best lot of 2-methylnaphthalene, some of the material described as lot 1 in table 5 was recrystallized twice from an equal volume of ethyl alcohol and the crystals were separated by centrifuging. After removal of the solvent, the "crystal" portion of this material had an initial freezing point of 34.415° C. The process of purification was repeated on this last portion, and a best lot was obtained which had an initial freezing point of 34.437° C. The time-temperature cooling curve of the best lot is shown in figure 8. On the basis of this curve, the amount of impurity in the best lot of 2-methylnaphthalene was estimated [6] to be 0.0000 ±0.0003 mole fraction.

The properties of the best 2-methylnaphthalene from petroleum are given in table 6, together with values of other investigators.

TABLE 6.—*Properties of 2-methylnaphthalene*

Material	From petroleum, Mair and Streiff		Evans [12]	Auwers and Frühling [11]
	(*A*) Actual "best" lot [a]	(*B*) Extrapolated to a purity of 100 percent		
Boiling point at 760 mm °C	[b] 241.14 ±0.05	241.14 ±0.05		
Boiling point at 57.78 mm °C	[b] 148.07 ±0.05	148.07 ±0.05		
Freezing point in air °C	34.44 ±0.01	34.44 ±0.02	34.5	31.5 to 32.8
Density at 40° C g/ml	[c] 0.99045 ±0.00002	0.99045 ±0.00005	1.008	0.9939
Refractive index at 40 °C n_C	[d] 1.59407 ±0.00010	1.59407 ±0.00010	1.6015	1.59444
Refractive index at 40 °C n_D	[d] 1.60192 ±0.00010	1.60192 ±0.00010		1.60258
Refractive index at 40 °C n_F	[d] 1.62306 ±0.00010	1.62306 ±0.00010		1.62390
Refractive dispersion at 40° C $n_F - n_C$	[d] 0.02899 ±0.00010	0.02899 ±0.00010		0.02946
Specific dispersion at 40° C $(n_F - n_C)/d$	0.02927 ±0.00010	0.02927 ±0.00010		0.0297

[a] Amount of impurity estimated to be 0.0000 ±0.0003 mole fraction.
[b] Determined by C. B. Willingham and F. D. Rossini.
[c] Determined by the Capacity and Density Section of this Bureau.
[d] Determined by L. W. Tilton of the Optical Instrument Section, of this Bureau.

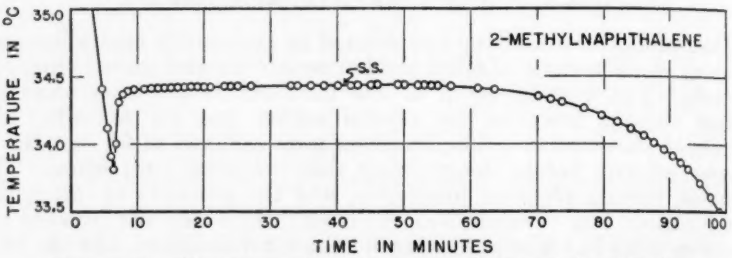

FIGURE 8.—*Time-temperature cooling curve for 2-methylnaphthalene.*

SS denotes the time at which the stirrer stopped. The scale of ordinates gives the temperature in °C. The scale of abscissas gives the time in minutes.

3. ISOLATION OF 1-METHYLNAPHTHALENE

For the isolation of 1-methylnaphthalene, all fractions on the 1-methylnaphthalene side of the eutectic of 1-methyl- and 2-methyl naphthalene were used, together with two distillation residues which, judging from their lower refractive indices, $n_D^{25}=1.594$ and 1.608, contained some mononuclear aromatics as impurities. This material was crystallized from alcohol and centrifuged in a manner similar to that employed with 2-methylnaphthalene. The volumes of the fractions obtained, percentages of impurities, and certain physical properties of the various lots of 1-methylnaphthalene are recorded in table 7. The percentage of the total distillate, 114° to 144° C at 56 mm Hg, constituted by the volume of 1-methylnaphthalene actually isolated, is recorded in table 9.

TABLE 7.—*Volumes and properties of the various lots of 1-methylnaphthalene actually isolated*

Lot	Volume	Refractive index at 25° C.	Freezing point in air	Amount of impurity [a]
	ml	n_D	*° C*	*Mole fraction*
1. Crystal I	90	1.6146	−31.02	0.0048±0.0011
2. Crystal II	100	1.6131	−33.5	.05 ±0.01
3. Crystal III	135	1.6113	−36.5	.11 ±0.02
4. Mother liquor	230	1.6016	−43.	

[a] Amount of liquid-soluble, solid-insoluble impurity, calculated from the lowering of the freezing point, using −30.77° C. (see table 8) as the freezing point of pure 1-methylnaphthalene and 2,250 cal/mole as its heat of fusion. This latter value was estimated by assuming the entropy of crystallization of 1-methylnaphthalene to be the same as that for 2-methylnaphthalene. The freezing point of a given lot was taken to be the highest temperature observed with crystals present. This temperature was attained at about 5 to 8 minutes from the start of supercooling. This would correspond to about 6 to 10 percent of the material frozen.

To obtain a best lot of 1-methylnaphthalene, the material labelled as lot 1 in table 7 was recrystallized twice from alcohol. The time-temperature freezing curve for the best 1-methylnaphthalene is shown in figure 9. On the basis of this curve, the amount of impurity in this

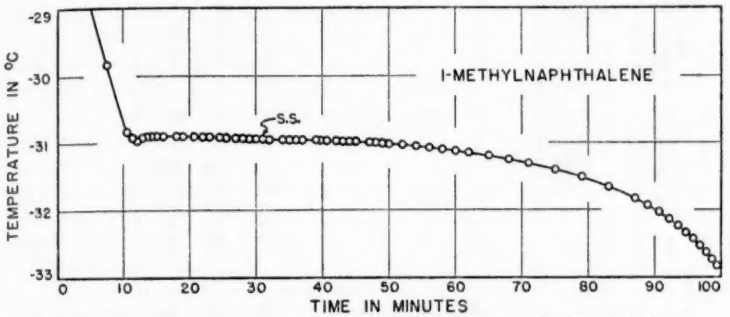

FIGURE 9.—*Time-temperature cooling curve for 1-methylnaphthalene.*

SS denotes the time at which the stirrer stopped. The scale of ordinates gives the temperature in ° C. The scale of abscissas gives the time in minutes.

best lot of 1-methylnaphthalene was estimated [6] to be 0.0025 ±0.0011 mole fraction, and the freezing point of pure 1-methylnaphthalene was estimated to be −30.77 ±0.06° C.

The properties of the best 1-methynaphthalene from petroleum are given in table 8, together with values previously determined for this substance.

TABLE 8.—*Properties of 1-methylnaphthalene*

Material	From petroleum, Mair and Streiff		Evans [12]	Auwers and Fruhling [11]
	(*A*) Actual "best" lot [b]	(*B*) Extrapolated to a purity of 100 percent		
Boiling point at 760 mm °C	[a] 244.78 ±0.10	244.78 ±0.10	244.4	
Boiling point at 57.8 mm °C	[a] 151.3 ±0.2	151.3 ±0.2		
Freezing point in air °C	−30.90 ±0.01	−30.77 ±0.06	−31	
Density [c] at 20° C g/ml	(1.0200) ±0.0002	(1.0200) ±0.0002	1.020	(1.0201)
Density [c] at 25° C g/ml	1.0163 ±0.0001	1.0163 ±0.0001	(1.016)	(1.016)
Refractive index [c] at 20° C n_D	(1.6175) ±0.0002	(1.6175) ±0.0002	1.6172	(1.6180)
Refractive index [c] at 25° C n_C	[d] 1.60677 ±0.00010	1.60677 ±0.00010		
Refractive index [c] at 25° C n_D	[d] 1.61494 ±0.00010	1.61494 ±0.00010	1.6145	
Refractive index [c] at 25° C n_F	[d] 1.63672 ±0.00010	1.63672 ±0.00010		
Refractive dispersion at 25° C n_F-n_C	0.02995 ±0.00010	0.02995 ±0.00010		(0.0300)
Specific dispersion at 25° C $(n_F-n_C)/d$	0.02947 ±0.00010	0.02947 ±0.00010		(0.0295)

[a] Values in parentheses were obtained by extrapolation, using for dn_D/dt and dD/dt the values 0.00051 and 0.00074, respectively. In the case of the data of Auwers and Fruhling, the extrapolation was made from 13.6° C.

[b] Amount of impurity (presumably 2-methylnaphthalene) estimated to be 0.0025 ±0.0011 mole fraction.

[c] Determined by C. B. Willingham and F. D. Rossini.

[d] Determined by L. W. Tilton of the Optical Instruments Section, of this Bureau.

XI. SUMMARY OF AMOUNTS OF MATERIAL PROCESSED, LOSSES DUE TO PROCESSING, AND AMOUNTS OF HYDROCARBONS ISOLATED

In table 9 there is given a summary of the material processed, the losses due to processing, the amounts of the hydrocarbons actually isolated, and estimates of the total amounts of these hydrocarbons in the petroleum. Columns 1, 2, and 3 identify the material processed and give the volume.

TABLE 9.—*Summary of the material processed, losses due to processing, and amounts of hydrocarbons isolated*[a]

No.	Material		Process	Product		Material lost in process		Amount of the product or of the given hydrocarbon actually isolated	Estimated amount of the given hydrocarbon not yet isolated	Total amount of the given hydrocarbon in the petroleum
	Name	Volume		Name	Volume	Volume	Percent			
		Liters			*Liters*	*Liters*	%	*Percentage of the distillate 114° to 144° C (at 56 mm Hg)*	*Percentage of the distillate 114° to 144° C (at 56 mm Hg)*	*Percentage of the distillate 114° to 144° C (at 56 mm Hg)*
I	Original distillate 114° to 144° C.	130.06								
II	Original distillate 127° to 133° C (from I).	38.81	Crystallization	*n*-Dodecane Mother liquors	14.91 23.14	0.76	2.0	11.7 ±0.05	1.9 ±0.8	13.6 ±0.8
III	Original distillate less *n*-dodecane removed (from II).	114.39	Extraction	Aromatic hydrocarbons Raffinate	21.11 87.96	5.32	4.7	17.1 71.2		
IV	Raffinate from extraction (from III).	87.96	Alternate adsorption plus extraction.	Aromatic hydrocarbons Naphthenes plus paraffins	2.40 82.59	2.97	3.4	2.0 69.2		
V	Aromatic hydrocarbons from extraction (from III and IV).	23.51	Distillation	Aromatic distillate fractions.	23.32	0.19	0.8	19.1		
VI	Stock used for naphthalene (from V).	0.644	Crystallization	Naphthalene Mother liquors	0.435 .132	.077	12.0	0.41 ±0.02 .12	0.05 ±0.03	0.46 ±0.04
VII	Stock used for 2-methylnaphthalene (from V).	2.150	Crystallization	2-Methylnaphthalene Mother liquors	1.432 0.535	.183	12.0	1.28 ±0.04 0.48	.5 ±0.2	1.78 ±0.21
VIII	Stock used for 1-methylnaphthalene (from V).	0.730	Crystallization	1-Methylnaphthalene Mother liquors	0.325 .230	.175	24.0	0.35 ±0.05 .25	.3 ±0.15	0.65 ±0.16

[a] See text for explanation.

Column 4 gives the fractionating process to which the material was subjected. Columns 5 and 6 give the name and volume of the products of the fractionating process. Columns 7 and 8 give the volume and percentage of the material lost in the given fractionating process. Column 9 gives the amount of the given hydrocarbon actually isolated, in percentage, based on the original distillate 114° to 144° C at 56 mm Hg as 100 percent. There are included in the values given in column 9 only those materials listed in tables 1, 3, 5, and 7 which had a purity better than 0.90 mole fraction. Column 10 gives an estimate of the amount of the given hydrocarbon not yet isolated, including material remaining in the mother liquors and in some of the distillation fractions which were not rich enough in the given hydrocarbon to crystallize profitably. Column 11 gives an estimate of the total amount of the given hydrocarbon in the petroleum, based on the original distillate, 114° to 144° C at 56 mm Hg, as 100 percent. The values given in columns 9, 10, and 11 were calculated in the following way. The volume of the original distillate, 130.06 liters, was taken as 100 percent at the start. The losses occurring in each process of fractionation were charged equally on a fractional basis to the products obtained from the given process. The losses were carried throughout in this cumulative way, so that at any given time the total volume of all the material on hand, including hydrocarbons isolated, remained 100 percent. In this way, the total material actually on hand, regardless of the losses which occurred, represented the original distillate, 114° to 144° C at 56 mm Hg.

XII. REVIEW OF EARLIER INVESTIGATIONS

Several earlier investigators established the presence in petroleum of the hydrocarbons whose isolation is described in the present paper. In some cases, these previous workers isolated the hydrocarbons by chemical means, but none obtained material of high purity by purely physical methods of separation, such as those used in the present work.

Shepard, Henne, and Midgley [7] prepared pure *n*-dodecane from a special fraction of petroleum extraordinarily high in normal paraffin hydrocarbons, by distillation, chemical treatment with chlorosulfonic acid, and redistillation.

Mabery and Hudson [13] found some Californian petroleums so rich in aromatic hydrocarbons that distillate fractions of the range 220° to 222° C at atmospheric pressure solidified on cooling to room temperature, because of the high concentration of naphthalene.

Jones and Wootton [14] established the presence in a Borneo petroleum of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene. The fractions distilling above 210° C at atmospheric pressure were treated with picric acid to obtain picrates. These picrates were separated and the hydrocarbon material was regenerated and recovered by steam distillation. The recovered hydrocarbon material was distilled, and naphthalene and the two methylnaphthalenes were recognized in the distillate fractions.

Birch and Norris [15] obtained naphthalene and 2-methylnaphthalene from a Persian petroleum. They used as a starting material the sulfur dioxide extract of the kerosene fraction, treated this with picric acid, separated the picrates, and regenerated and fractionally distilled the hydrocarbon material. Crystalline naphthalene separated from

the fractions boiling at 215° to 230° C, and 2-methylnaphthalene was obtained from the fractions distilling at 237° to 245° C by cooling to −21° C. Both of these hydrocarbons were purified by crystallization from alcohol. Their attempts to separate the picrate of 1-methylnaphthalene were not successful.

Tasaki and Yamamoto [16] likewise obtained naphthalene and 2-methylnaphthalene. They steam-distilled the sulfuric acid sludge from a Shukkoko kerosene, and fractionally distilled the oil obtained. On cooling the fractions, naphthalene and 2-methylnaphthalene crystallized from some of them.

Cosciug [17], using the picric acid method with a Rumanian petroleum, obtained picrates which he identified as those of naphthalene and 2-methylnaphthalene. By fractional crystallization of the picrates from ethyl alcohol, followed by distillation of the regenerated hydrocarbons, he was able to obtain pure 2-methylnaphthalene but not pure 1-methylnaphthalene.

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CONCERNING THE EXISTENCE OF FRACTIONS OF THE SERICIN IN RAW SILK

By Henry A. Rutherford and Milton Harris [1]

ABSTRACT

The question of the possible existence of several fractions of the sericin of raw silk has been investigated. The relative yields of sericins *A* and *B*, obtained after treatment of silk in an autoclave, were found to be dependent on the duration of the treatment. Practically all of the sericin removed in the early stages of autoclaving was in the form generally designated as sericin *B*. On continuing the treatment, this fraction was rapidly converted into the more soluble form, sericin A. Analyses of the fractions obtained after autoclaving the silk for different lengths of time showed that the alleged sericins *A* and *B* are not definite chemical entities, but are substances whose chemical compositions vary with the duration of the autoclave treatment. The results of the investigation show that the sericin fractions are artifacts, which result from the hydrolytic decomposition of the naturally occurring sericin during its removal from the fiber.

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I. INTRODUCTION

Raw silk fibers consist of at least two proteins, silk fibroin and silk sericin. The latter forms a coating over the fibroin and constitutes 15 to 30 percent of the total weight of the raw fiber. Removal of sericin from fibroin is based on the solubility of the former in hot aqueous solutions. The solubility increases considerably in the more alkaline or acid solutions.

A variety of concepts relative to the nature of sericin and the fractions obtained from it have appeared in the literature. In 1784 one of the first published records on the removal of sericin from silk by the use of alkaline solutions appeared [1][2]. A number of similar investigations followed until Cramer [2], in 1865, expanded the scope of the investigations and obtained several proteins by fractionation of

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation, Inc.
[2] Numbers in brackets indicate literature references at the end of this paper.

a solution of sericin. He suggested that these fractions were decomposition products of the naturally occurring material. Following his findings, Wetzel [3], Bondi [4], Fischer and Skita [5], and Anderlini [6], studied the removal of sericin from silk and concluded that sericin in raw silk exists in more than one modification, although good experimental evidence to substantiate such a conclusion was lacking. In the above-mentioned investigations, different procedures for the preparation of the sericin solutions were employed, and little analytical work was done to characterize the protein fractions which were obtained. As a consequence, widely different results were reported by the different investigators. For example, Bondi found two fractions in a solution of sericin obtained by boiling silk in water, while Anderlini was able to separate three fractions after a prolonged extraction of raw silk with water at 50° to 60° C.

More recently, Shelton and Johnson [7] isolated two fractions from sericin solutions which had been obtained by autoclaving raw silk in water at temperatures of about 115° C. They concluded that raw silk sericin contains at least two proteins, one of which is soluble and the other insoluble in cold water. Subsequent investigators, using the autoclave to remove the sericin, appeared to substantiate these findings, and also attempted to define the properties of the isolated fractions. Mosher [8] stated that both fractions are very much alike chemically but possess different physical properties, especially with respect to solubility. He further noted that the insoluble fraction was converted into a soluble one by boiling in aqueous solution, the conversion being greatly accelerated by increasing the acidity, alkalinity, or temperature of the solutions. Although he concluded that sericin is composed of three distinct fractions, his results could be interpreted to mean that sericin does not exist as a mixture of proteins in raw silk, and that these fractions are decomposition products formed during the process of removal of the sericin from the fibers.

In contrast to some of the conclusions of Mosher, Kaneko [9], and Ito and Komori [10] found the different sericin fractions to be different chemically. Their results were based on determinations of the nitrogen distribution and the tyrosine contents of the isolated fractions. However, disagreements are found even between the data of these investigators. For example, Kaneko found that the soluble fraction is especially rich in arginine nitrogen, whereas Ito and Komori found a greater proportion of this nitrogen in the insoluble portion.

From consideration of the previous investigations, it became evident that no satisfactory conclusion concerning the existence of several fractions of the sericin of raw silk could be reached. In the present investigation an attempt was made to throw further light on the question by making a more extensive study of sericin and of the fractions obtained from it.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS AND METHODS

Samples of white Japanese silk which had received no previous treatment other than that used in the reeling process were used in this work. The naturally occurring waxes were removed by cold extractions for 24 hours each with alcohol and ether. Analyses of the dewaxed fiber gave the values shown in table 1. The data for sericin

were calculated from the analytical data for the dewaxed silk and fibroin and from the determined sericin content.

Total nitrogen was determined by the microKjeldahl method, and tyrosine by Lugg's method [11], after an alkaline hydrolysis. The amino-nitrogen content of the fibrous and of the insoluble proteins was determined by the method of Rutherford, Harris, and Smith [12]. The method of Van Slyke [13] was used for the determination of the amino-nitrogen content of sericin solutions. Carbohydrate and amino sugars were estimated by the methods outlined by Sørensen [14, 15].

TABLE 1.—*Total and amino-nitrogen, tyrosine, carbohydrate, and amino-sugar contents of the dewaxed silk, fibroin and sericin used in the present investigation*

The data for sericin were calculated from the analytical data on dewaxed silk and fibroin and from the determined sericin content.

Material	Total nitrogen	Amino nitrogen [a]	Tyrosine	Carbohydrate (as glucose)	Amino sugars (as glucosamine)	Sericin content
	%	%	%	%	%	%
Dewaxed silk	18.29	0.14	10.9	0.67	0.80	23.7
Fibroin	18.73	.09	12.3	.56	.30	----
Sericin	16.92	.30	6.3	1.0	2.4	----

[a] Determined by method of Rutherford, Harris, and Smith [12].

2. PREPARATION OF SERICIN SOLUTIONS

Most of the sericin solutions used in this work were prepared by an autoclaving method similar to that described by other investigators [7, 8, 10]. The raw silk was placed in a beaker of water at about 100° C in the autoclave, the ratio of fiber to water being 1 to 50. Steam was passed into the autoclave until a temperature of 114° to 115° C was reached. Approximately 5 minutes was required for this operation. The temperature was then maintained by addition of more steam for the duration of the treatment. The silk was removed from the solution, squeezed, and immediately rinsed in one 500-ml portion of water at 90° C. As much liquid as possible was squeezed from the silk and combined with the rinse solution and the solution obtained after autoclaving. The combined solutions were then rapidly cooled to room temperature in a water bath.

3. FRACTIONATION OF THE SERICIN

In earlier work, the fractionation of the sericin in solution was accomplished by the use of alcohol or ammonium sulfate, but in more recent work, most investigators have preferred to use different buffer solutions. It was found necessary, however, to redetermine the pH for maximum precipitation as the values reported in the literature [8, 10] vary from pH 3.6 to 4.1. A preliminary experiment was made on a solution of sericin, prepared by a 30-minute treatment in the autoclave. The solution was brought to room temperature and aliquots of it were immediately adjusted to definite pH values in the range from 3.5 to 4.3 with acetate buffers of constant ionic strength (0.02 *M*). After 15 hours, the precipitated protein was centrifuged off, and the total nitrogen content (a measure of the protein remaining in solution) and the pH of the supernatant liquid were determined.

A considerable portion of the protein was precipitated in the pH range used, but maximum precipitation appeared to occur at pH 4.0. In all subsequent fractionation experiments, the solutions were adjusted to this pH and allowed to remain in a refrigerator overnight before removal of the insoluble protein.

The fraction which is insoluble at pH 4 was separated from the remainder of the solution with a centrifuge. The precipitate was thoroughly washed with fresh portions of the acetate buffer, then with alcohol and with ether, and finally dried for 4 hours in a vacuum oven at 50° C.

The acetate washings were added to the solution remaining after centrifuging, and the whole was evaporated to a small volume by passing a stream of air over it at room temperature. The protein in the concentrate was precipitated by addition of the solution to a sufficient volume of alcohol (95 percent) at about 0° C, to make the final concentration of alcohol 75 percent. The precipitate was separated from the solution with a centrifuge, washed with alcohol and with ether, and dried in the vacuum oven for 4 hours at 50° C.

The solution remaining after the separation of the protein which was insoluble in 75-percent alcohol was combined with the alcohol and ether washings from both sericin fractions, evaporated to dryness on the steam bath, and the weight of the residue determined. The solid material was dissolved in a small amount of water, the solution diluted to 25 ml, and suitable aliquots were taken for nitrogen, tyrosine, and carbohydrate determinations.

4. DESIGNATION OF THE SERICIN FRACTIONS

The authors do not intend to perpetuate, in future papers, the use of the following terms for the designations of the sericin fractions. These terms, which were adopted by previous investigators, are used in this paper merely for convenience and to avoid further confusion. Sericin *B* is the fraction of the protein which is insoluble at pH 4. The fraction which is soluble at pH 4 but insoluble in a 75-percent solution of alcohol is called sericin *A*. In the present investigation, a small fraction soluble in a 75-percent solution of alcohol was also found. For convenience, this material is referred to as sericin *D*, although in a series arranged in descending order with regard to solubility, it should precede sericin *A*. The existence of another fraction, sericin *C*, has been reported and described by Mosher [8] as extremely insoluble.

III. RESULTS AND DISCUSSION

The effects on dewaxed silk of varying the duration of the autoclave treatment are shown in table 2 and figure 1. About 80 percent of the total sericin of the silk is removed in as little time as 20 minutes; practically complete removal is accomplished in approximately 1 hour. The yields of sericins *A* and *B* are seen to vary considerably with the duration of autoclaving. Of the total sericin removed during treatment of dewaxed silk for 5 minutes, more than 97 percent was in the form of sericin *B*. The yield of this fraction decreased, however, as the duration of the autoclave treatment was increased until, after 3 hours, only 18.7 percent of the total sericin was recovered in this

form. On the other hand, the very low yield of 2.7 percent of sericin *A*, obtained during the 5-minute treatment, was increased to 77.4 percent by 3 hours in the autoclave. Only a small amount of sericin *D* was present. As is shown in the last column, practically all of the sericin in solution was accounted for.

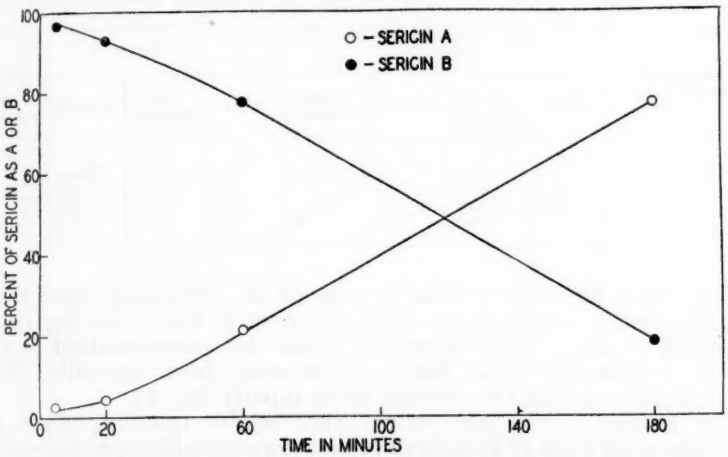

FIGURE 1.—*Effect of duration of autoclaving on the yields of sericins A and B.*

TABLE 2.—*Effect of duration of autoclaving on the yields of sericin A, B, and D*

Duration of autoclaving	Loss in weight of dewaxed silk	Sericin *B*	Sericin *A*	Sericin *D*	Total extracted sericin accounted for
min	%	%	%	%	%
5	12.6	97.1	2.7	Trace	99.8
20	18.9	93.3	3.7	1.1	98.1
60	21.1	77.5	21.2	1.3	100.0
180	22.9	18.7	77.4	3.8	99.9

The data clearly show that sericin *A* is a decomposition product of the naturally occurring sericin, and is formed during the autoclave treatment. If, however, fraction *A* were present in the native raw silk, it would be expected that it would be more rapidly removed, because of its high solubility. Actually, the sericin samples obtained in the shortest times of autoclaving (5 to 20 minutes) were practically entirely in the form of sericin *B*.

Further evidence supporting the conclusion that the fractions of sericin result from decomposition produced during autoclaving of the fibers is found in the analytical data of the different fractions, as shown in table 3. *The data show that sericins A and B as obtained under these conditions are not definite chemical entities but are substances whose chemical compositions vary with the length of the autoclave treatment.* A comparison of these data with the calculated total and amino nitrogen, and tyrosine contents of sericin in dewaxed silk (table 1) indicates that the sericin *B* fraction, obtained from silk during autoclaving for only 5 minutes, is probably very similar to the undegraded

sericin. This similarity and the fact that more than 97 percent of the sericin removed in this time is sericin *B* strongly suggest that all of the sericin in raw silk is present in one form.

TABLE 3.—*Nitrogen and tyrosine contents of the sericin fractions obtained from dewaxed silk during autoclaving for different lengths of time at 115°C*

Duration of autoclaving	Sericin *B*				Sericin *A*			
	Yield	Total nitrogen	Tyrosine	Amino nitrogen	Yield	Total nitrogen	Tyrosine	Amino nitrogen
min	%	%	%	%	%	%	%	%
5	97.1	16.87	6.2	0.32	2.7	13.94	Trace	.....
20	93.3	17.00	6.5	.....	3.7	15.68	2.5	.....
60	77.5	17.23	6.5	.....	21.2	16.44	5.1	.....
180	18.7	16.44	5.4	.45	77.4	16.67	6.5	0.49

Since the bulk of the sericin is removed in a relatively short time, and practically entirely in the form of sericin *B*, the increasing yields of sericin *A* must result principally from the decomposition of the sericin *B* after the latter has been removed from the silk. This decomposition appears to proceed fairly rapidly (fig. 1).

The increase in the yield of the very soluble fraction, sericin *D*, with increased time of autoclaving, as shown in table 4, is indicative of even more extreme decomposition of the sericin. The chief interest in this fraction is found in its relatively high carbohydrate and amino-sugar contents. The samples obtained after 20 minutes contain about three times as much of these substances as the original sericin. It should be noted, however, that although there is a fourfold increase in yield of sericin *D* when the duration of the autoclave treatment is extended from 20 to 180 minutes, there is only a comparatively small increase in the total yields of amino sugar and carbohydrate. In other words, the first of these very soluble decomposition products is relatively rich in these substances, but the subsequent fractions of the sericin contain appreciably lower amounts.

TABLE 4.—*Effect of the duration of the autoclave treatment on the yield of sericin D*

Duration of autoclave treatment	Yield[a] of sericin *D*	Carbohydrate (as glucose)	Amino sugar (as glucosamine)
min	*mg*	*mg*	*mg*
20	102	4.7	4.0
60	134	6.4	6.1
180	432	7.4	6.9

[a] Yield from 50 g of dewaxed silk.

The data in table 3 also show that the conversion of sericin *B* to *A* is accompanied by an increase in amino-nitrogen content, sufficient to account for an appreciable amount of hydrolysis. Additional evidence that hydrolytic decomposition occurs during treatment of sericin with boiling water was obtained in the following experiment. A sample of dewaxed silk was placed in boiling water and aliquots of the resulting sericin solution were removed at different time intervals

for the determination of total and amino nitrogen. The results are presented in figure 2, and show that hydrolysis of the sericin proceeds at an appreciable and fairly constant rate.

No attempt has been made to isolate the sericin *C* fraction because, as shown above, none of the isolated fractions has any particular significance as regards the sericin as it exists in the raw silk.

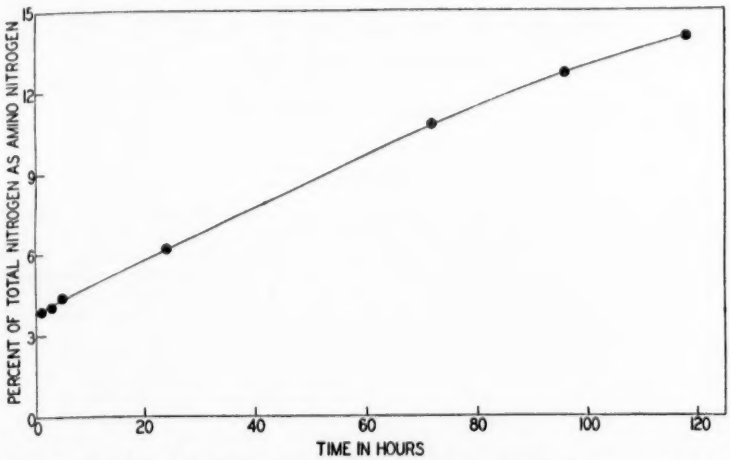

FIGURE 2.—*Rate of increase of the amino-nitrogen content of a sericin solution during prolonged treatment at 100° C.*

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[15] Sørensen, Compt. rend. trav. lab. Carlsberg. Sér. chim. **22,** 487 (1938).

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METHODS OF MEASURING pH IN ALKALINE CYANIDE PLATING BATHS[1]

By Maurice R. Thompson

ABSTRACT

For many years the pH of acid plating baths has been measured and controlled, especially in nickel plating, but only recently has attention been given to similar control of alkaline cyanide baths. It is more difficult to apply either the electrometric or the colorimetric method to the accurate measurement of these baths, mainly because of uncertainty as to salt error. In the work described, comparative readings were made on buffered alkaline sodium chloride solutions (1 to 3 *N*) with the hydrogen electrode (which is free from salt error by definition), with a commercial bulb-type glass electrode, and with three colorimetric sets. Readings of pH by the glass electrode were too low by about 0.5 to 1.5 pH unit. Readings with the indicators were usually too high by about 0.5 to 1.0 pH unit, varying with the indicator. The glass electrode error increased both as the salt content and pH of a solution increased. The colorimetric error also increased as the salt content of a solution increased, but at a lesser rate than for the glass electrode. The colorimetric error decreased, however, as the pH increased.

Corrections to readings of the glass electrode and of the indicators on several cyanide copper plating bath samples, in which the hydrogen electrode could not be used, were made on the assumption that salt errors of alkaline chloride and cyanide are the same. The corrected readings by the two methods agreed within 0.5 pH. More extensive measurements would be desirable, however, before adopting definite corrections for the large errors involved. It seems desirable, therefore, to continue to report uncorrected pH values for alkaline cyanide plating solutions, stating the type and make of apparatus employed. The condition of glass electrodes should be checked occasionally, for example, by reading the pH of a buffered solution with a salt content comparable to that of the samples being measured and with a true pH value established by the hydrogen electrode.

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[1] A preliminary report upon this investigation, entitled "The Measurement of pH in Alkaline Cyanide Plating Baths", was presented to the Twenty-seventh Annual Convention and International Conference of the American Electroplaters' Society at Asbury Park, N. J., June 19 to 22, 1939, and was printed in the Convention Proceedings.

I. INTRODUCTION

For more than 15 years it has been customary to measure and control the pH of nickel-plating baths,[2] which are usually operated in the acid range, but only recently has this test been applied to alkaline cyanide baths,[3 4 5] such as those of copper, brass, silver, zinc, and cadmium. With nickel-plating baths, the pH was found to be one of the factors affecting current efficiency and the character of the deposit. Similar effects have also been reported for the cyanide baths. In controlling these cyanide baths, two questions naturally arise: (1) How concordant and how accurate are the present methods of measurement? (2) What are the favorable limits of pH for the operation of a given bath? At the present time there is little information available for answering the first question, to which the present paper is confined.

Both electrometric and colorimetric methods are now in use for measuring the pH of plating baths. The colorimetric method requires less experience and, for a limited range of pH, less investment in apparatus. The electrometric method, in one form or another, is applicable to a wider range of conditions, is suitable for automatic recording if this is required, and is free from the personal equation and eye fatigue which are associated to some extent with color matching.

Early experience with nickel baths showed that the indicators used in the colorimetric method were subject to "salt errors," which caused a discrepancy between the results of this and the electrometric method. By the salt error of a pH measurement is meant any deviation of either the electrometric or colorimetric reading, in a solution containing a high concentration of salts, from the value (the "true pH") that would have been obtained in that solution with a hydrogen electrode (if applicable). The hydrogen electrode as the primary standard has a zero salt error by definition. The difference between this true pH and that observed by any other method for the same solution gives the salt error and therefore the correction to be applied to the observed pH.

Blum and Bekkedahl[6] found that usually with nickel baths the pH values obtained by the indicators were consistently too high by about 0.5 unit. Therefore the subtraction of 0.5 pH from the colorimetric values made them concordant with hydrogen electrode readings. (Fortunately in this case the hydrogen electrode was applicable to sufficiently pure nickel solutions. Also, the quinhydrone electrode had a negligible salt error in nickel solutions.) The recording of such corrected values facilitates the comparison of the results obtained by various investigators with different methods. The present investigation was designed to ascertain whether a similar standardization of methods could be applied to measurements of the pH of alkaline cyanide solutions.

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[5] A. K. Graham and H. J. Read, Metal Ind. (New York) **35**, 559 (1937); **35**, 617 (1937); **36**, 15 (1938); **36**, 77 (1938); **36**, 120 (1958); and **36**, 169 (1938).
[6] W. Blum and N. Bekkedahl, Trans. Am. Electrochem. Soc. **56**, 291 (1929).

II. PRINCIPLES INVOLVED

If it were possible to measure the pH of a metal cyanide solution with a hydrogen electrode, a comparison of this value with that obtained by any other method would show directly the error of the other measurement. The hydrogen electrode, however, is not applicable in metal cyanide solutions, as it is subject to disturbance by metal reduced upon it and to "poisoning" by cyanide. Unfortunately, there is no other electrode now available which is altogether satisfactory for these solutions. The quinhydrone electrode gives erroneous readings above pH 9; and the antimony electrode has many limitations, including disturbance by traces of copper salts. The glass electrode, perfected recently as a durable commercial device, has the disadvantage of an increasingly large sodium-ion error above pH 10. (The potassium-ion error is comparatively small, and the barium-ion error is almost negligible. Most cyanide plating baths however, are now prepared from sodium cyanide.) It has usually been considered, however, that this error is fairly reproducible when a uniform technique is employed. Moreover, it has been reported that the glass electrode is free from specific anion effects, that is, the sodium-ion error for 1 N Na^+ is the same whether sodium chloride, sulfate, phosphate, or other salt, is employed.

This situation led to the use in this investigation of the glass electrode as a secondary electrometric standard for the cyanide baths. Comparative measurements with the hydrogen and glass electrodes can be made in alkaline "buffered" solutions prepared with known high concentrations of such salts as sodium chloride or sodium sulfate. The difference in readings gives the sodium-ion error and hence the correction for the glass electrode. The assumption is then made that equivalent concentrations of sodium cyanide or of double sodium metal cyanides would affect the glass electrode reading to the same extent in plating solutions. (If these were not freshly prepared baths of known formula, the total sodium content could be determined by standard methods of analysis.) Then by applying the previously determined corrections, to such readings, corrected values approximating the true pH values of the plating bath samples are obtained. This procedure also involves the assumption that heavy metal compounds have no appreciable effect on the glass electrode measurements in alkaline solutions (no effect has been found in acid solutions). This appeared to be the most practicable electrometric procedure at present, although the numerous assumptions made and the difficulties involved in making glass electrode measurements in alkaline solutions tend to make the results at best only approximate.

The situation with respect to the colorimetric method is very similar. The commercial indicator sets are calibrated by means of standard buffer solutions, which are dilute (except in the upper alkaline range), and the pH of which has been measured with the hydrogen electrode. The indicator sets are graduated in 0.2 pH intervals and normally give values that are correct within ± 0.1 pH for similar dilute solutions, but not for solutions with high salt contents. Cyanide plating baths have fairly high concentrations of double cyanide, free sodium cyanide, sodium carbonate, and other salts. The effect of such salts, at a given pH, is to shift the color of the indicator, usually toward the alkaline side. As with the glass electrode, this error is

readily determined for solutions in which the true pH value can be measured by the hydrogen electrode, for instance in concentrated chloride or sulfate solutions. The corresponding correction of colorimetric readings on cyanide baths also involves the assumption that cyanide causes about the same salt error with indicators as does an equivalent concentration of other salts. Unfortunately, there are few data available on the specific salt errors of indicators.[7] It is probable that these errors are correlated more directly with the ionic strength of a solution than with the salt concentration. As no high accuracy is required for the present purposes, however, the salt concentration will be used and, as will appear, it seems suitable as a first approximation.

Experimentally, it is found that the sodium-ion error of the glass electrode is negative in the alkaline range, that is, the observed pH reading is too low. The salt error of the indicators is commonly (but not always) positive, and thus the observed pH reading is ordinarily too high. The true pH is, therefore, generally between these two values but usually not exactly midway between them. These relations may be summarized as follows:

1. Hydrogen-electrode reading (if practicable)=true pH.
2. Glass electrode reading+glass electrode sodium-ion error=corrected pH (approximately the true pH).
3. Colorimetric reading−indicator salt error=corrected pH (approximately the true pH).
4. Glass electrode reading+glass electrode sodium-ion error=colorimetric reading−indicator salt error. Consequently, if the pH of a given cyanide bath is determined from a corrected glass electrode reading and also from a corrected colorimetric reading, the two results, if correct, should agree. Any difference between them indicates the present degree of uncertainty in the methods employed and in the assumptions made.

III. DETERMINATION OF SALT ERRORS

The various steps used to determine the salt errors of the instruments employed in this investigation may be summarized briefly as follows.

1. ELECTROMETRIC MEASUREMENTS

(a) HYDROGEN ELECTRODE

Readings were made on all of the buffer solutions and buffered salt solutions with the hydrogen electrode. Platinized platinum-foil electrodes were used in conjunction with saturated calomel reference electrodes in a suitable cell, which was placed in an air bath kept at a temperature of 25° C±0.2°. The electromotive force of the reference electrode was taken as 0.2458 volt. The hydrogen was purified by passage through heated palladium-asbestos and then presaturated with water vapor in a bubbling tube. Readings were corrected for barometric pressure in the usual manner. Borate buffer solutions with and without added salts were employed. All solutions were stored in waxed bottles.

[7] W. W. Scott, Standard Methods of Chemical Analysis, [ed. 5] 2, 2274 (Chapter on Determination of pH by the Colorimetric Method by W. A. Taylor and F. R. McCrumb). (D. Van Nostrand Co., Inc., New York, N. Y., 1939.)

(b) GLASS ELECTRODE

Several makes [8] of commercial portable pH meters, or pH electrometers, are now available for use in the control of cyanide plating baths. These consist essentially of an electron-tube potentiometer, to which is connected an electrode chain of a bulb-type glass electrode and a saturated calomel electrode. The sample of solution is placed in a small movable cup which surrounds the glass electrode. The potentiometer scale can be read by estimation to ± 0.01 pH.

For this investigation a Coleman Model 3–D electrometer was used, with several extra Coleman glass electrodes (made of Corning 015 glass) for comparative readings when necessary. The scale of the Coleman potentiometer was checked by comparison with a precision potentiometer, after substituting a resistance of 200 megohms for the electrode chain. (This instrument has only one scale, which is adjustable by means of a switch for either pH or millivolt readings.) The asymmetry potential of the glass electrode was balanced with 0.05 *M* acid potassium phthalate buffer solution (prepared from standard sample 84a of the National Bureau of Standards), for which the pH was taken as 3.97.[9] Glass-electrode measurements on buffer solutions, on buffered salt solutions, and on plating samples were usually made at 25° C. (The Coleman instrument, however, contains a compensating device which automatically corrects for potential shift of the electrodes with temperature.)

The handling of a glass electrode included two rinses with distilled water and two rinses with the sample to be measured, followed by a reading within 5 minutes. Frequent attention was given to flushing the liquid junction and to balancing the asymmetry potential against the phthalate buffer. The glass electrodes were kept in distilled water when not in use.

2. COLORIMETRIC MEASUREMENTS

Because the available colorimetric sets differ in the indicators employed and in the construction of the color standards, it was desirable to include several makes in this investigation. Equipment and indicators were lent by Hellige, Inc. (H), by LaMotte Chemical Products Co. (L), and by W. A. Taylor & Co. (T). The Hellige standards consist of colored glass disks mounted on a small wheel, the LaMotte Standards are separate ampoules used in a holder, and the Taylor standards are small ampoules mounted in separate slides for each indicator. All these sets are graduated at 0.2 pH intervals and under good conditions can be read to ± 0.1 pH. The indicators used with each set and the various ranges of pH are listed under the name of the maker in table 1. (Other indicators furnished for the lower alkaline range were not required for the present investigation.)

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[8] Among these are the instruments supplied by the Coleman Electric Co.; Hellige, Inc.; Leeds & Northrup Co.; and the National Technical Laboratories.

[9] This is the value given by W. M. Clarke, "The Determination of Hydrogen Ions" [ed. 3], p. 486 (Williams & Wilkins Co., Baltimore, Md., 1928). It is probable that this value will shortly be revised to pH 4.01 in accordance with work done at the National Bureau of Standards and other laboratories. Such a change, however, is too small to affect the results given in this paper.

TABLE 1.—*Colorimetric sets*

pH range	Hellige (H) indicators	LaMotte (L) indicators	Taylor (T) indicators
10.0 to 11.6	Nitro yelow	Nitro yellow	Tolyl red.
11.0 to 12.6		Sulpho orange	Parazo orange.
11.2 to 12.8	Tropaeolin O		
12.0 to 13.6	Violet	Violet	Acyl blue.

The original calibrations of these three colorimetric sets were checked by readings on buffer solutions which were prepared by partly neutralizing 0.1 *N* NaOH with 0 to 0.2 *M* H_3BO_3, and with few exceptions the standards were found to be correct within the reproducibility of the observations. These and the subsequent colorimetric readings were made at about 25° C by two or more observers, and the readings usually agreed within 0.2 pH, with an average deviation of about 0.1 pH. The indicator sets were then employed to measure the pH of the same buffered salt solutions and plating solution samples as were used with the glass electrode.

IV. DISCUSSION OF MEASUREMENTS

1. HYSTERESIS OF GLASS ELECTRODE

It was noted that a glass electrode of the type employed was subject to a lag or hysteresis when used in concentrated alkaline salt solutions. For instance, higher pH values were obtained for a series of solutions measured in the order of increasing salt content than when measured in the order of decreasing salt content. The maximum discrepancy observed was about 0.1 pH. This effect is probably connected with the difficulty of displacing the film of solution on the surface of the glass by another solution of different concentration. Thus, Perley [10] has stated: "The glass surface is highly adsorptive. When changing from a buffer solution to an unbuffered solution, considerable washing is required. The thicker and more robust the glass electrode, the greater must be the degree of washing."

Hysteresis was minimized by thorough rinsing, by making measurements in the same order of concentration, and by checking the asymmetry potential before each reading.

2. VARIATION BETWEEN DIFFERENT GLASS ELECTRODES

Previous investigators [11] have reported agreement within 0.05 pH for several commercial bulb-type glass electrodes of the same make. In this investigation, less close agreement was usually obtained. The electrodes used were not especially selected for the same age and condition. Differences of 0.1 pH or more were encountered, when the same buffered alkaline chloride solution was measured, especially in the upper range of pH. Such discrepancies, which are difficult to explain, may be connected with variations in the rate of attack of alkaline solutions upon the glass of different electrodes. This subject of attack has been studied by Hubbard, Hamilton, and Finn.[12] In the present investigation the most concordant electrodes were found to be those used frequently under similar conditions.

[10] G. A. Perley, Am. Dyestuff Reptr. **26,** 832 (1937).
[11] W. C. Gardiner and H. L. Sanders, Ind. Eng. Chem., Anal. Ed. **9,** 274 (1937).
[12] J. Research NBS **22,** 339 (1939) RP1187.

3. "PSEUDOANION" EFFECT UPON GLASS ELECTRODE

The fact that glass electrodes have usually been considered free from specific anion effects has been mentioned. However, most of the research on glass electrodes has been done with the membrane type, which is comparatively small, thin, and very sensitive. In this investigation, it was found that the salt error with sodium sulfate solutions was slightly lower than with sodium chloride solutions. This effect

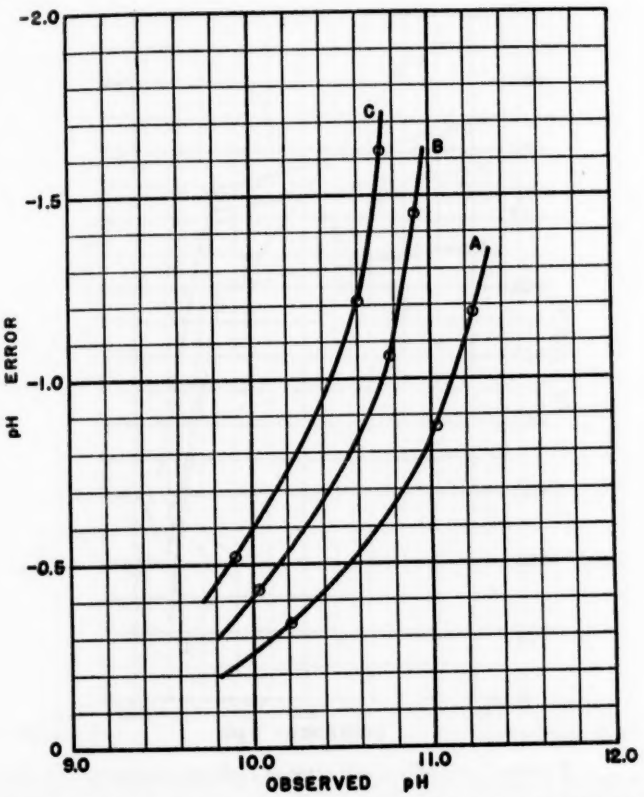

FIGURE 1.—*Typical sodium error of a bulb-type glass electrode, for chloride solutions: A, 1 N* Na; *B, 2 N* Na; *C, 3 N* Na.

might be related to differences in adsorption, or in rate of attack, or both, for the two solutions. If commonly found with bulb-type electrodes, it could be regarded as a "pseudoanion" effect until more information is available.

The combination of hysteresis, variation between different electrodes, and pseudoanion effect may make a combined uncertainty in the reading of bulb-type glass electrodes in concentrated alkaline solutions of several tenths of a pH unit, especially in the upper range of pH where the salt error changes rapidly. Figure 1 shows typical results for the sodium-ion error of a glass electrode that has fairly high sensitivity in the upper pH range. These results apply only to

the buffered sodium chloride solutions, in which the error is relatively large. The curves for other individual electrodes would not necessarily coincide with those of figure 1.

4. COLORIMETRIC MEASUREMENTS

The colorimetric measurements were closely reproducible. The indicators used for the upper pH range, however, are "one-color"

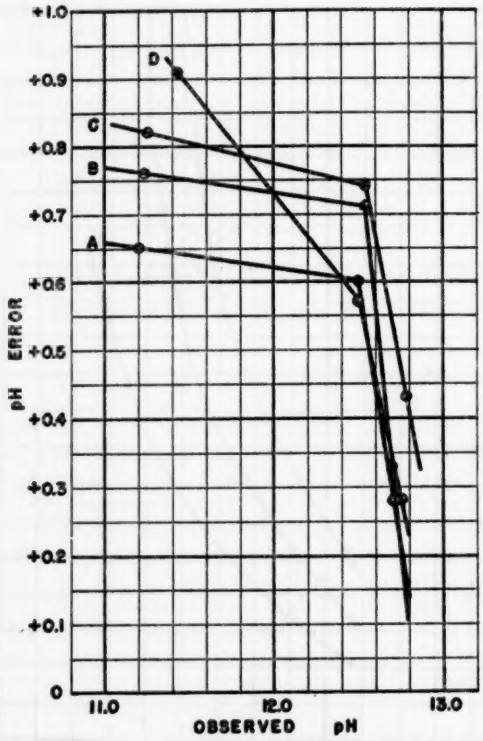

FIGURE 2.—*Sodium salt error of Hellige indicators.*

For chloride solutions: *A*, 1 *N* Na; *B*, 2 *N* Na; *C*, 3 *N* Na. For sulfate solution: *D*, 2 *N* Na.

dyes and are more difficult to compare than the "two-color" dyes employed for the acid range of pH. In general, comparisons with a violet or blue dye were found to be less sharp than with one having a pink or yellow color.

With few exceptions, the indicators for a given set had salt errors of the same order of magnitude, which did not increase rapidly above 1 *N* Na^+. The curves for salt error plotted against observed pH were of the same general shape and are shown in figures 2, 3, and 4 for the individual sets. (Where the readings of different indicators of a

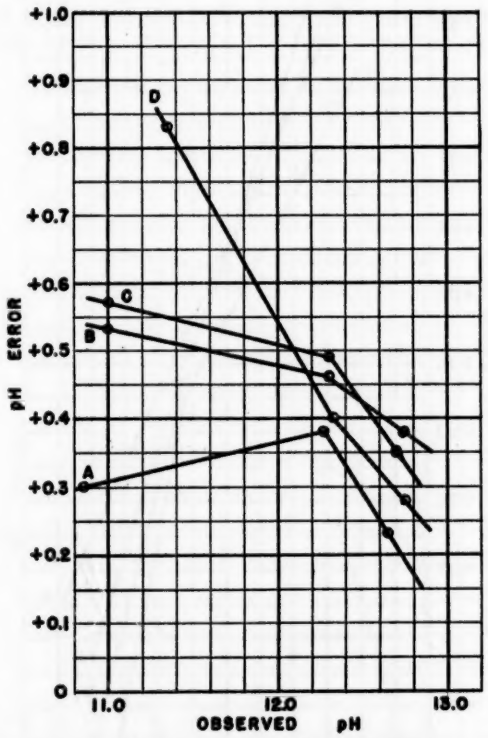

FIGURE 3.—*Sodium salt error of LaMotte indicators.*

For chloride solutions: *A*, 1 *N* Na; *B*, 2 *N* Na; *C*, 3 *N* Na. For sulfate solution: *D*, 2 *N* Na.

set overlapped, they agreed closely enough to warrant using averaged values for the points shown.) This situation made possible the combination of the results for each set into the generalized curve shown in figure 5, which, like figure 1, is based only on the buffered sodium chloride solutions. These generalized curves are reliable to about ±0.2 pH, which is sufficient for the present purpose. With some indicators, sulfate had a greater effect than chloride in the lower part of

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the pH range. All of the indicator curves showed a sharp decrease in error above pH 12, where the error approached zero. It was pointed out by F. R. McCrumb [13] that this result is caused by the necessity

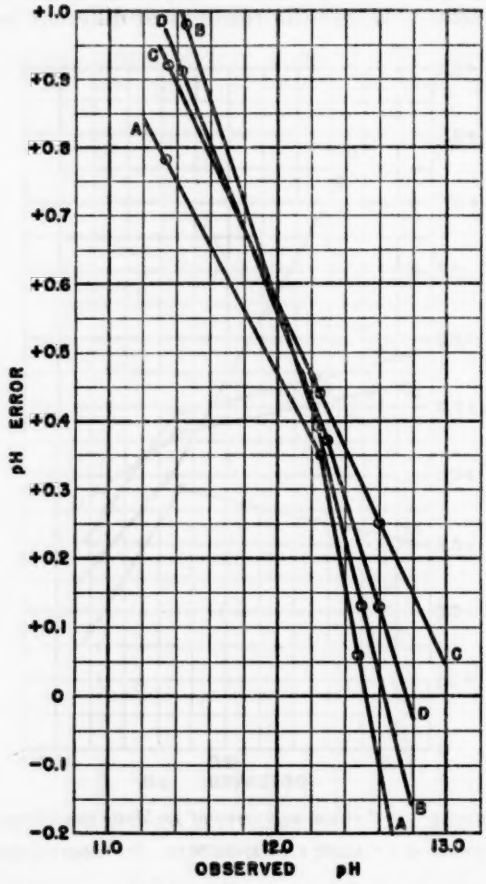

FIGURE 4.—*Sodium salt error of Taylor indicators.*

For chloride solutions: *A*, 1 *N* Na; *B*, 2 *N* Na; *C*, 3 *N* Na. For sulfate solution: *D*, 2 *N* Na.

of calibrating the upper pH standards against solutions of fairly high sodium hydroxide content. At this end of the scale the color and rated pH for the indicator correspond, therefore, more closely to the concentrated than to the dilute salt solutions.

[13] Chemical Director, W. A. Taylor & Co., Inc. Private communication.

V. APPLICATION OF THE RESULTS TO THE pH MEASUREMENT OF CYANIDE COPPER PLATING BATHS

A few solutions were prepared to represent cyanide copper plating baths, for testing the applicability of the proposed methods. Copper baths were selected because they are used extensively and are occasionally kept under pH control. Two types, a regular cyanide and a Rochelle salt bath, were prepared from chemicals of known purity.

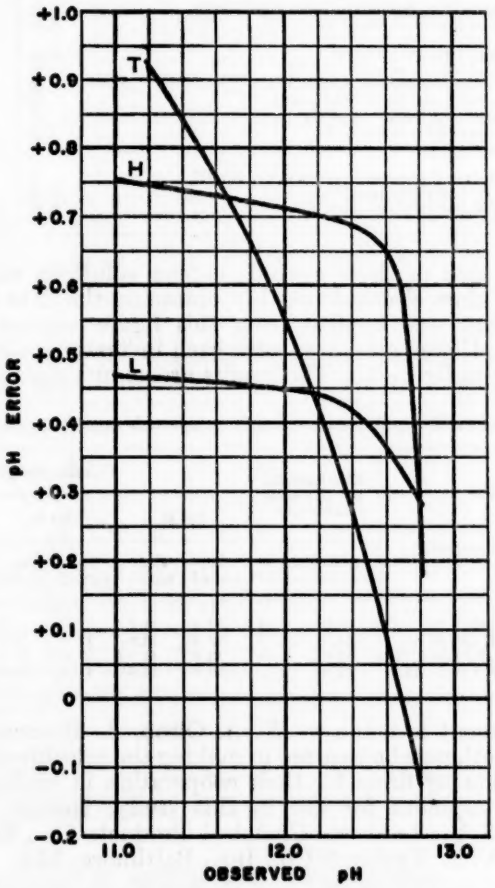

FIGURE 5.—*Generalized sodium salt error of indicators for chloride solutions of 1 N* Na *or greater: Hellige (H); LaMotte (L); Taylor (T).*

A portion of each was also adjusted to a higher pH value by adding sodium hydroxide. These portions furnished for measurement four solutions which had the compositions given in table 2.

TABLE 2.—*Composition of copper baths*

Designation	Compounds	Concentration		
		N	g/liter	oz/gal
A	Copper cyanide, CuCN	0.25	23	3
	Total sodium cyanide, NaCN	.65	34	4.5
	(Free sodium cyanide), NaCN	.15	7.5	1
	Sodium carbonate, Na_2CO_3	.30	15	2
	Total sodium content, Na	.95		
B	Solution *A* plus sodium hydroxide, NaOH	.10	4	0.5
	Total sodium content, Na	1.05		
C	Copper cyanide, CuCN	0.34	30	4
	Total sodium cyanide, NaCN	.77	38	5
	(Free sodium cyanide), NaCN	.09	4.5	0.6
	Rochelle salt, $NaKC_4H_4O_6.4H_2O$	.32	45	6
	Sodium carbonate, Na_2CO_3	.57	30	4
	Total sodium content, Na	1.50		
	Total potassium content, K	0.16		
D	Solution *C* plus sodium hydroxide, NaOH	.10	4	0.5
	Total sodium content, Na	1.60		
	Total potassium content, K	0.16		

The pH of each of these cyanide copper solutions was measured with the same glass electrode used in obtaining the data for figure 1, and a correction was applied from this figure whenever possible. Similarly, the pH was measured with each indicator set and a correction applied from figure 5. The results are summarized in table 3.

TABLE 3.—pH *measurements on cyanide copper baths*

Bath		Electrometric pH (By glass electrode)		Colorimetric pH					
				Set H		Set L		Set T	
Designation	Composition	Observed	Corrected	Observed	Corrected	Observed	Corrected	Observed	Corrected
A	Regular; 0.95 *N* Na	10.8	11.4	12.4	11.7	11.9	11.4	11.9	11.3
B	*A*+NaOH; 1.05 *N* Na	11.3	12.7	12.8	12.6	12.9	12.6	12.7	12.7
C	Rochelle salt; 1.50 *N* Na	10.9	11.9	12.6	11.9	12.0	11.5	12.0	11.5
D	*C*+NaOH; 1.60 *N* Na	11.6		12.8	12.6	13.0	12.8	12.8	13.0

Acknowledgment is made to W. A. Olson, A. Brenner, P. W. C. Strausser, and others who assisted in making the colorimetric readings; and to the following firms for their cooperation in lending extensive colorimetric equipment for use in this study: Hellige, Inc., Long Island City, N. Y.; LaMotte Chemical Products Co., Towson, Baltimore, Md.; W. A. Taylor & Co., Inc., Baltimore, Md.

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SOME OBSERVATIONS ON DETERMINING THE SIZE OF PORES IN PAPER

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ABSTRACT

The various methods which have been used to determine the size of pores in paper are briefly reviewed. These are of three general types: (a) methods based on rate of efflux of fluids; (b) methods based on rate of rise of liquids in vertical strips; (c) methods based on the capillary pressure involved in penetration by liquids.

A new method is outlined, which takes advantage of the fact that the coefficient of slip of air in viscous flow through paper is a function of pressure. From the Meyer equation, the average effective pore radius is evaluated in terms of the air permeability values at two pressures. It is only necessary to determine the air permeability at two different pressures of an identical area of paper. Experimental values for two such air-permeability determinations on each of five papers, and the resulting values calculated for the average effective pore radius, are tabulated.

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I. METHODS AVAILABLE

1. INTRODUCTION

A number of attempts have been made to determine the size of the pores in paper. It may seem pointless even to broach the question of the size of the pores in such a structure, inasmuch as the free spaces in the network of fibers that constitute a sheet of paper are extremely irregular and indefinite in shape and size. The fact remains, however, that much effort has been expended in attempting to assign some

numerical value to characterize the size of the pores in paper and various other materials. And the effort seems justified, both by the practical usefulness of such a numerical characterization and by the behavior of the materials. Although there is probably no such thing in a sheet of paper as a long, cylindrical capillary tube, the sheet, nevertheless, behaves in certain respects as if its system of pores were made up of a large bundle of such capillary tubes in parallel, making it possible to talk about and write equations for a system of pores that behaves in certain respects like the system of pores in an actual sheet of paper. It is very necessary, of course, that one keep in mind the limitations of such a contrivance. Let us suppose, for instance, that the channels are interconnected within the body of the sheet, as they possibly are in most papers. One might then, with good reason, look upon the whole network as a single pore, and pore size from such a viewpoint might not have any relation to pore size as defined from a different point of view.

2. TACIT DEFINITION

Most of the efforts that have been made to determine the size of pores in paper have concerned themselves with the behavior of fluids flowing within the structure of the sheet, and it is from this point of view that pore size has been tacitly defined by many workers. The values arrived at, of course, tell us little more than the average size, or the range of sizes, in a system of simple pores amenable to mathematical treatment which would behave, toward the flow of fluids, like the actual system of pores in the sheet. The sheet of paper does not necessarily contain any actual structural counterpart of the capillary system evaluated. The values for size of pores thus obtained have, nevertheless, been considered very useful in certain applications of paper and other porous materials. Some investigators have tried to interpret the results more nearly in accordance with reality by applying correction factors to accord with particular types of structure [3, 9, 10].[1]

3. THE MICROSCOPE AS AN AID

The microscope is a valuable means of studying the pore structure of paper. It does not, however, give the same type of information as do flow measurements. It does not readily reveal which spaces are the pores or continuous channels, or how the spaces at different levels are connected. It is difficult to analyze the complex pattern that one sees in a magnified cross section of paper and to appraise it in terms of pores available for the transfer of fluids through the structure.[2] Although the dimensions seen with the microscope are highly significant as supplementary evidence, they cannot be regarded as having cardinal significance over values for pore size obtained through flow measurements. One cannot hope that they will do more than confirm the order of magnitude of values determined from actual flow measurements.

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] A possible aid in this difficulty may be found in the suggestion of Dr. McPherson, of the Bureau staff, that a small amount of a gas, such as hydrogen selenide or hydrogen telluride, be mixed with the air that is being forced through the paper. Such a gas reacts with cellulose to dye it a distinctive color, which might aid one in tracing the air passages by sectioning the paper and examining it with a microscope.

4. METHODS BASED ON RATE OF EFFLUX OF FLUIDS

The estimation of pore size in paper through flow measurements has occupied the attention of several investigators during the past decade. Baird and Hrubesky [1] outlined methods of approach based on the work of Stamm [15] on wood sections. They proposed to make air-permeability measurements and apply the familiar Poiseuille equation, whereby the average effective radius, r (as defined by these workers), can be calculated from the permeability of the paper and the number and length of the capillaries in an equivalent system of parallel cylindrical capillaries. For necessary simplicity they assumed (as have other workers) the length of the air passages to be equal to the thickness of the paper.[3] Since the number of pores, N, is unknown, it was necessary to obtain, in addition to the Poiseuille equation, a second equation relating the average radius to the number of pores. Such an equation was formulated by determining the fractional pore area (equal to $\pi r^2 N$ per unit area of the sheet) as the ratio of the conductivity of a concentrated electrolyte saturating the paper to the conductivity of a free volume of the electrolyte equal to the volume of the paper.[4]

Although Baird and Hrubesky did not present definite values for pore size by their method, they gave values for pore space relative to the total air space, which indicate their belief that not more than 2 percent of the air spaces in a sheet of paper are continuous passages through the sheet available for the transfer of air. This would require the pores to be relatively large in order to account for the air permeability.

It may be of interest to note that Edwards [5], using the same general procedure on leather, estimated the average effective radius of the pores to be about 0.5 to 1 micron (thousandth of a millimeter) for the samples studied. He evaluated the fractional pore area by means of water-vapor–permeability data.

Manegold and Solf [9] made use of a somewhat similar procedure. They made permeability measurements with liquids and with air, expressing the results as specific permeability. They evaluated the fractional pore area as the ratio of the volume of liquid required to saturate a piece of paper, to the volume of the paper. Their values for the average effective pore radius of various papers ranged from 0.0007 to 8 microns, with values of a few tenths of a micron for most ordinary papers.

5. METHODS BASED ON RATE OF ASCENT OF LIQUID IN STRIPS

It has been shown that under certain conditions the radius of the bore in a glass capillary is proportional to the square of the height to which a liquid that wets it will rise in a given time [8, 19]. Simmonds [14], after presenting data to show that certain papers behave approximately in conformity with this relation when strips are hung with the lower end in water, applied this equation to evaluating the size

[3] The effective length of the pores through paper is almost certainly many times the thickness of the paper. In a previous publication [4] it was pointed out that the behavior of paper in air-permeability measurements demands a comparatively long path through the sheet. The fact that most fibers in paper are much flattened as a result of the pressure applied in calendering suggests that the channels between fibers may be likened to the spaces in a pile of overlapping flat plates. A fluid flowing down through such a structure would have to follow a very tortuous course back and forth between the surfaces of the plates, covering a distance many times the height of the pile. That part of the fluid traveling within the fibers of a sheet of paper would also follow a long path, since the fibers are nearly parallel to the plane of the paper.

[4] The electrolytic method of determining the fractional pore area was later repudiated by Stamm [16].

of the pores. He reported values for the average effective radius of the pores in cartridge paper board as about 0.008 to 0.045 micron; in blotting paper, about 0.1 to 0.3 micron; in sulfite pulp sheets, about 0.5 micron.

Foote [6] extended the experiments of Simmonds, using formamide, alcohol, and benzene, in addition to water. His experiments were made on sulfite bond, from a part of which the rosin sizing had been extracted so that readings could be obtained with water and formamide. His values for the average effective radius of the pores ranged from 0.006 to 0.35 micron, depending upon the liquid used in the experiments of capillary rise. He pointed out, however, that it may not be valid to assume that the contact angle is zero in all cases, and also that the equation used is probably not valid when the paper swells while the liquid is flowing through its structure. He considered his highest values (obtained with alcohol) to be the most credible.

Peek and McLean [13] measured the rate of rise of six organic liquids in strips of filter paper, and showed that the experimental data fitted their derived equation for the rate of rise. By evaluating the constants of their equation they were able, on the assumption of a uniform distribution of sizes, to calculate the range of pore sizes. They reported the values of 4 to 40 microns as the range of effective capillary radii of the filter paper with which they experimented. They included photomicrographs of cross sections of the filter paper to show that the widths of spaces presumed to be pores appear to lie within these limits.

6. METHODS BASED ON CAPILLARY PRESSURE

Larocque [7] forced oil at different pressures through paper and measured the time of transudation in each case. He then evaluated the capillary pressure by extrapolating the plot of pressure against the reciprocal of time to the zero value of the reciprocal of time to obtain a value for the pressure necessary to prevent penetration (pressure at infinite time of transudation). He then calculated the average effective capillary radius from the familiar equation of elementary physics, whereby the radius is twice the ratio of the surface tension of the liquid to the capillary pressure, for a liquid that wets the capillary. The value reported for the average effective pore radius in a supercalendered book paper was about 5 microns; in a bond paper, about 10 microns.

A modification of this procedure, involving the air pressure necessary to expel a liquid saturating a sheet of paper, was suggested by Baird and Hrubesky [1] as a means of evaluating the maximum pore radius of paper.

7. OTHER DATA AND METHODS

Witzmann [20] determined the average effective pore radius in filter paper and other filtering media, using several of the methods which have been outlined. He reported values for filter paper ranging from 0.05 to about 6 microns, depending on the method used and on the grade of filter paper tested.

Similar methods have been applied to the determination of pore size in other materials [2, 15, 17], and also an additional one involving the Kelvin relation of the curvature of a liquid in a capillary (and

hence the radius of the capillary, when small) to the vapor pressure over the curved surface. This method, however, does not appear to have been adapted to the estimation of pore size in paper.

It is apparent from the foregoing review that it has been necessary to make liberal use of simplifying assumptions in evaluating pore size in paper, and that there is still some uncertainty about the order of magnitude of the size of the pores in this material.

II. A NEW METHOD

1. ORIGIN OF THE METHOD

In 1934 the writer found a more direct method of estimating the average effective pore size in a porous material, which does not appear to have been used before, and in view of the interest which has been manifested in the subject since that time, it seems desirable to describe it.

Bureau Research Paper RP682 [4] reported data showing that, by various criteria, the passages in a sheet of paper, through which air flows under a pressure difference across the sheet, behave as if they were a bundle of long capillary tubes in parallel. However, the effect of atmospheric pressure, or total pressure on air permeability did not seem to fit this interpretation. In this work Meyer's [11] equation for the efflux of a gas from a capillary tube was used, with the customary omission of the term containing the slip coefficient, inasmuch as for most situations it is valid to assume that the movement of the layer of fluid in contact with the walls of the capillary is so small as to be negligible. A short time after the paper was published, Guy Barr, of the National Physical Laboratory in England, pointed out that, whereas the omission of the term containing the slip coefficient would make no perceptible difference in evaluating the effect produced by other variables studied, it might make a difference in the case of a change in total pressure if the capillaries were small enough, inasmuch as the slip coefficient is a function of pressure. The data were reexamined in the light of Dr. Barr's suggestion, and it was found that a very probable value of the average effective pore radius could be obtained from the pressure-permeability data.

This interpretation of the total-pressure effect renders some of the conclusions in RP682 about this variable subject to revision, and brings into harmony all of the criteria used as evidence of the nature of the air passages in paper. It is not necessary to assume an elastic expansion of voids to explain the behavior, since the pressure criterion is no longer useful, inasmuch as an increase in air permeability with decreasing total pressure may be expected, regardless of the nature of the capillaries, when they are small enough.

2. SLIP COEFFICIENT

The Meyer equation for the viscous flow of a gas may be written

$$VP=\frac{\pi r^4 tD(2P-D)}{16L\eta}\left(1+\frac{4s}{r}\right), \tag{1}$$

in which V is the volume of gas, measured at the inlet pressure, P, which, in the steady state of efflux, enters the capillary in time, t, under a constant pressure difference, D, between the two ends; r is the radius of the capillary; L is its length; η is the coefficient of

viscosity; and s is the coefficient of slip, which Meyer defines as the ratio of the coefficient of viscosity to the coefficient of friction on the walls of the capillary. Ordinarily the wall friction is so great that a layer of gas remains substantially fixed on the walls of the capillary, and the coefficient of slip becomes negligibly small in most applications of the equation. Actually, however, there is a slight movement, or slipping, of this surface layer in the direction of the gas stream, and it is this circumstance that affords the means to be described of estimating the size of the pores in paper. When r is small enough s/r cannot be neglected, and in paper we seem to have pores small enough to require that the slip factor be dealt with.

3. EQUATION FOR PORE RADIUS

The air permeability of paper is defined as the volume of air (measured at the inlet pressure) which flows through a unit area of the paper in unit time per unit pressure difference (the pressure difference used being always small in comparison with the total pressure). If, now, the average effective pore radius is defined as the radius of one of N identical cylindrical capillaries of length L in parallel, which, in combination, have the same air permeability as the paper under identical conditions, this air permeability, A, can be written

$$A=\frac{NV}{tD}=\frac{N\pi r^4}{8L\eta}\left(1-\frac{D}{2P}\right)\left(1+\frac{4s}{r}\right). \tag{2}$$

At some other inlet pressure, P', the air permeability, A', for a pressure difference, D' can be written in a similar manner. Dividing one equation by the other gives

$$\frac{A'}{A}=\frac{r+4s'}{r+4s}\cdot\frac{2PP'-PD'}{2PP'-P'D'} \tag{3}$$

since η is not a function of pressure. The last part of eq 3 will drop out, either when D and D' are so small in comparison with P and P' that the term is unity within experimental error (as was the case in the previous work) or when D and D' are chosen so that $PD'=P'D$.

The slip coefficient, s, is proportional to the mean free path of the molecules of the gas, and, in fact, is approximately equal to it [12]. That is, s is inversely proportional to the total pressure, or $sP=s'P'$. Therefore, from eq 3, with D and D' chosen as prescribed,

$$r=4s\frac{AP/P'-A'}{A'-A}. \tag{4}$$

If we take the slip coefficient equal to the mean free path, then s has a value of about 10^{-5} cm (0.1 micron), when P is 1 atmosphere. One has, therefore, only to make two determinations of the air permeability of a piece of paper at different total pressures, in order to calculate the average effective pore radius. Since from the form of eq 4, it is immaterial what unit is chosen for A and A', the air permeability will be reported in the customary unit.

4. EXPERIMENTAL VALUES

The apparatus used in determining the effect of change in total pressure, and described in RP682, was of the dual, differential-pressure type, with provision for changing the total pressure about 10 percent.

The calibration of the flowmeter would not be altered significantly by the change in total pressure in these experiments, because the radii of the glass capillaries used are large in comparison with the mean free path.

It may be well to emphasize that the experimental determination of the air permeability with this apparatus does not depend in any way upon the Meyer equation, and hence that a large ratio of slip coefficient to radius does not imply doubt about the accuracy of the determination. The equation was used in the previous work only as a means of interpreting the behavior of the paper. The values of A are subject to an uncertainty of probably less than 1 percent. The values of A', on the other hand, are probably somewhat more uncertain because of the increased difficulties of making the measurements, and because of possibly significant changes in testing conditions, such as in relative humidity resulting from the change in total pressure.

Table 1 gives the values obtained for the average effective pore radius calculated for 5 different papers by eq 4 from air-permeability measurements at two values of total pressure. These results are not inconsistent with evidence afforded by the microscope, and appear to be very probable values for the order of magnitude of the size of pores in paper. The values for the coated papers probably characterize the pore structure of the coating rather than of the paper that supports the coating. The relatively small air permeability of the bond paper, considering the size of its active pores, probably results from a marked decrease in the number of active pores, brought about by the plugging of most of the smaller passages with the glue sizing, which is normally concentrated near the surface in a bond paper.

TABLE 1.—*Average effective pore radius*

[Calculated from air-permeability measurements at two values of the total pressure, that is, for two values of the slip coefficient]

Paper	Air permeability in $\frac{\text{cm}^3/\text{sec}}{\text{m}^2\ (\text{g/cm}^2)}$		Average effective pore radius,
	A at 1 atm	A' at 0.9 atm	r
			Microns
Double-coated book paper	3.20	3.45	0.2
Single-coated book paper	6.95	7.40	.3
Ledger paper	37.5	39.0	.8
Machine-finished book paper	156.5	161.0	1.2
Bond paper	8.90	9.15	1.2

5. CONCLUDING REMARKS

It is not unlikely, as is suggested by the work of some of the investigators mentioned previously, that the effective size of the pores may be different for the three primary axes of paper. The results in table 1 are for flow normal to the plane of the sheet. It should not be difficult to devise an apparatus, making use of a mercury envelope, such as has been used by Stull and Johnson [18], with which air-permeability measurements at different pressures could be made in the lengthwise direction of strips of paper.

Although the method which has been outlined is applicable at ordinary pressures only to porous materials having a limited range of sizes of pores, it should be possible to extend the range by operating at low pressures, where the mean free path becomes correspondingly larger. The experimental difficulties would, of course, be increased, and a number of variables would come into more prominence.

With improvement in apparatus and technique, the slip-coefficient method of estimating pore size should be not without promise among the several less direct methods of approach which are available to investigators interested in learning more about the structural characteristics of paper and other porous materials.

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OUTDOOR EXPOSURE TESTS OF ELECTROPLATED NICKEL AND CHROMIUM COATINGS ON STEEL AND NONFERROUS METALS

By William Blum and P. W. C. Strausser [1]

ABSTRACT

This paper includes the results and conclusions of extensive atmospheric exposure tests conducted since 1936 through cooperation of the American Electroplaters' Society, American Society for Testing Materials, and the National Bureau of Standards. Exposure tests of coatings of copper, nickel, or chromium, or combinations of these metals, plated upon steel, copper, brass, zinc, and zinc-base die-castings were made in six locations. The thickness of the nickel layers was found to be the most important factor in the value of the coatings for protection against corrosion.

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I. INTRODUCTION

In 1932, atmospheric exposure tests of plated coatings on steel were initiated by a joint committee of the American Electroplaters' Society, American Society for Testing Materials, and National Bureau of Standards.[2] In 1936, similar tests were started with plated coatings on various nonferrous metals,[3] and in 1938 these were supplemented with some additional coatings.[4] In the 1936 and 1938 exposures, some new plated steel specimens were also included in order to confirm and extend the earlier observations on steel. This paper summarizes the results obtained in these tests since 1936. While some of the specimens may be exposed for longer periods, especially in the milder locations, it is believed that subsequent observations upon them will not materially alter the conclusions based upon the exposures up to the present time.

II. PREPARATION OF SPECIMENS

1. BASIS METALS

All of the specimens were flat sheets or plates 4 by 6 in. (10 by 15 cm). Most of the rolled metals were No. 22 gage (0.031 in., or 0.78 mm), and the cast metals were from 0.1 to 0.2 in. (2.5 to 5 mm) thick. The types and compositions of all the basis metals are listed in table 1.

[2] W. Blum, P. W. C. Strausser, and A. Brenner, *Protective value of nickel and chromium plating on steel*, J. Research NBS **13**, 331 (1934) RP712.
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W. Blum, P. W. C. Strausser, and A. Brenner, *Corrosion protective value of electrodeposited zinc and cadmium coatings on steel*, J. Research NBS **16**, 185 (1936) RP867.
[3] Report of joint committee, Proc. Am. Soc. Testing Materials **36**, pt. 1, 212 (1936).
[4] Report of joint committee, Proc. Am. Soc. Testing Materials **38**, pt. 1, 250 (1938).

TABLE 1.—*Composition of base metals*

Number	Basis metal	Number of sets	Description of basis metal	Composition, by analysis				
A. FERROUS METALS								
				Carbon	Manganese	Phosphorus	Sulfur	Silicon
				%	%	%	%	%
I	Steel	12	Cold-rolled (SAE No. 1010)[a]	0.10	0.43	0.006	0.017	[b] 0.01
II	do	2	Full cold-rolled	.07	.39	.013	.034	[b] .01
III	do	2	Spring, rolled	.83	.66	.023	.026	.17
IV	Iron	2	Gray, cast	3.46	.48	.64	.08	2.82
V	do	2	Malleable, cast	1.64	.27	.12	.13	0.93
B. COPPER AND COPPER ALLOYS								
				Copper	Lead	Tin	Aluminum	Manganese
				%	%	%	%	%
VI	Copper	4	Deoxidized, sheet	99.9				
VII	Brass	7	Cast high (ASTM B65-28)[c]	60.9	2.6	1.0	0.32	
VIII	do	3	Cast low-ounce metal (ASTM B62-28)[d]	85.4	5.5	4.7		
IX	do	3	Extruded (ASTM B16-29)[e]	62.3	2.9	[b] 0.05		
X	do	18	Rolled high (ASTM B36-33)[f]	65.7	[b] 0.1			
XI	do	4	Rolled low (alloy L, Com. B-3)[g]	85.0				
XII	Nickel-brass	5	Rolled (Fed. Spec.)[h]	64.6				0.23
XIII	do	5	Cast (Fed. Spec.)[h]	66.5	3.7	3.4		

				Nickel	Iron	Zinc
				%	%	%
VI	Copper	4	Deoxidized, sheet		[b] 0.01	
VII	Brass	7	Cast high (ASTM B65-28)[c]	[b] 0.05	[b] .05	35.1
VIII	do	3	Cast low-ounce metal (ASTM B62-28)[d]		[b] .01	4.4
IX	do	3	Extruded (ASTM B16-29)[e]	[b] .05	[b] .1	34.6
X	do	18	Rolled high (ASTM B36-33)[f]		[b] .01	34.2
XI	do	4	Rolled low (alloy L, Com. B-3)[g]		[b] .01	15.0
XII	Nickel-brass	5	Rolled (Fed. Spec.)[h]	18.2	[b] .2	16.8
XIII	do	5	Cast (Fed. Spec.)[h]	18.9	[b] .2	7.2

C. ZINC AND ZINC ALLOYS

				Zinc	Copper	Aluminum	Iron	Lead	Magnesium
				%	%	%	%	%	%
XIV	Zinc	6	Rolled	98.4	0.99		0.017	0.62	
XXI	Zinc alloy	7	Die-cast (ASTM alloy No. XXI)[i]	93.8	2.2	4.0	.009		0.02
XXIII	do	21	Die-cast (ASTM alloy No. XXIII)[i]	96.1		3.9	.005		.04

[a] SAE Handbook, Soc. Auto. Engrs., p. 254 (1936).
[b] Less than.
[c] Standard Specifications for Yellow Brass Sand Castings for General Purposes (ASTM designation B 65), 1933 Book of ASTM Standards, pt. 1, p. 597.
[d] Standard Specifications for Composition Brass or Ounce Metal Sand Castings (ASTM designation B 62), 1933 Book of ASTM Standards, pt. 1, p. 612.
[e] Standard Specifications for Free-Cutting Brass Rod for Use in Screw Machines (ASTM Designation B 16), 1933 Book of ASTM Standards, pt. 1, p. 719.
[f] Standard Specifications for Sheet High Brass (ASTM Designation B 36), 1933 Book of ASTM Standards, pt. 1, p. 728.
[g] Report of Committee B-3 on Corrosion of Non-Ferrous Metals and Alloys, Proc. Am. Soc. Testing Materials, **32**, pt. 1, 218 (1932).
[h] Federal Specification for Builders' Hardware, Lock and Lock-Trim (FF-H-106).
[i] Zinc was determined by difference.
[j] Tentative Specifications for Zinc-Base Alloy Die Castings (ASTM designation B86-34T) Proc. Am. Soc. Testing Materials, **34**, pt. 1, 706 (1934); also 1935 Book of ASTM Tentative Standards, p. 369.

2. PREPARATION FOR PLATING[1]

The basis metals were received from the manufacturers with one or both sides polished, and generally were not subjected to further polishing. However, the zinc-base die-castings were given a light "color buffing" to remove the slight tarnish that had developed in storage. All specimens were carefully inspected before plating, and those with visible surface defects were rejected.

Before plating the specimens, they were subjected to appropriate cleaning and dipping operations. In general, the specimens were subjected to the following cycle of operations: (1) removal of grease with organic solvents, (2) cathodic cleaning in an alkaline solution, (3) rinsing in water, (4) dipping in acid, and (5) rinsing in water. If the first plating was to be done in a cyanide copper solution, the rinsed specimens were dipped into a solution containing 30 g/liter (4 oz/gal) of sodium cyanide and again rinsed. The conditions used in these operations are given below.

(a) USE OF ORGANIC SOLVENTS

The 1936 specimens were merely dipped into carbon tetrachloride. The 1938 specimens were cleaned in a vapor degreaser with stabilized trichloroethylene.

(b) CATHODIC CLEANING

The solutions and conditions for cleaning each basis metal are listed in table 2. A small amount, about 0.1 g/liter, or 0.01 oz/gal, of liquid soap was added to each cleaning solution to reduce the formation of spray.

TABLE 2.—*Cathodic cleaning of metals*

Basis metal	Solution composition								Temperature		Current density		Time
	Na_2CO_3		Na_3PO_4		Na_2SiO_3		NaOH						
	g/liter	*oz/gal*	*g/liter*	*oz/gal*	*g/liter*	*oz/gal*	*g/liter*	*oz/gal*	*°C*	*°F*	*amp/dm²*	*amp/ft²*	*sec*
Steel and iron	30	4	30	4	------	------	4	0.5	90	195	5	50	60
Copper and brass	15	2	15	2	8	1	4	.5	90	195	2	20	120
Zinc alloys	23	3	23	3	------	------	------	------	90	195	2.5	25	30
Buffed nickel	15	2	15	2	------	------	4	.5	75	170	3.5	35	15

(c) DIPS

(1) *Steel and iron.*—Each metal was dipped into the acid designated in table 3 for a period sufficiently long to produce a slight visible etching. After pickling the cast-iron specimens they were scrubbed with pumice and water to remove any loose graphite.

Sets 102 and 182 were pickled cathodically in 2 *N* sulfuric acid (7.5 fl oz/gal) at 50° C (120° F) for 2 minutes at 2 amp/dm² (19 amp/ft²). Lead anodes were used.

(2) *Copper and brass.*—In general, the copper and brass specimens were cleaned in the solution designated in table 2, rinsed, dipped into 1 *N* hydrochloric acid (13 fl oz/gal) at room temperature, and rinsed again.

[1] P. W. C. Strausser, Monthly Rev. Am. Electroplaters' Soc. 23, No. 10, 23 (1936).

TABLE 3.—*Pickling of steel and iron*

Basis metal	Composition of solution				Temperature		Time
	Sulfuric acid		Hydrochloric acid				
	H_2SO_4	Com. acid 95%; sp gr 1.84	HCl	Com. acid 32%; sp gr 1.16			
	g/liter	*fl oz/gal*	*g/liter*	*fl oz/gal*	*°C*	*°F*	*sec*
Cold-rolled steel I	98	7			50	120	120
Cold-rolled steel II	98	7			50	120	15
Spring steel III			73	25	25	75	15
Gray cast iron IV	98	7			50	120	10
Malleable cast iron V	98	7			50	120	8

Instead of being dipped into hydrochloric acid, two sets (C 3 and B 43) were etched anodically in ammonium citrate.[6] The ammonium citrate solution was prepared by neutralizing 50 g of citric acid with ammonium hydroxide, adding 20 g of citric acid, and diluting to 1 liter. Etching was conducted at room temperature for 1 minute, with an anodic current density of 1 amp/dm² (9 amp/ft²).

On sets B 6, B 45, B 54, and B 55, anodic etching was conducted at room temperature in *N* sulfuric acid (3.5 fl oz/gal) for 2 seconds at 1 amp/dm² (9 amp/ft²). Even this short treatment sometimes left a dark film on the surface, which was removed by swabbing with water.

One set of brass (B 59A) was dipped for 2 seconds into a "bright dip" of the following composition:

Bright dip	ml/liter	fl oz/gal
Sulfuric acid, H_2SO_4 (sp gr 1.84)	530	68
Nitric acid, HNO_3 (sp gr 1.42)	160	20
Hydrochloric acid, HCl (sp gr 1.19)	.8	.1
Water, H_2O	320	40

Even this short dip etched the surface so much that the nickel deposits, after buffing, were not as bright as the regular buffed-nickel coatings.

The nickel-brass specimens were prepared like the brass except that, after the alkaline cleaning, they were scrubbed with pumice and water. When chromium was to be deposited directly on the nickel-brass, the metal was dipped into 2 *N* sulfuric acid (7 fl oz/gal) instead of into hydrochloric acid.

(3) *Zinc and zinc-base die-castings.*—After cleaning and rinsing the 1936 specimens, they were dipped into 0.5 *N* hydrochloric acid (6 fl oz/gal) until effervescence just started over the entire surface. For rolled zinc, this required about 2 seconds; for die-casting XXI, 3 seconds; and for XXIII, 5 seconds.

The 1938 specimens of XXI and XXIII alloys were dipped for 25 seconds into 0.7 *N* sulfuric acid (2.5 fl oz/gal).

[6] A. W. Hothersall, *The adhesion of electrodeposited nickel to brass*, J. Electrodepositors' Tech. Soc. 7, 115 (1932).

3. CONDITIONS USED IN PLATING

The plating baths and operating conditions are listed in tables 4 to 7. The specimens were held in racks so designed that, except near the edges, the thickness of each deposit was uniform within ±5 percent, as determined by microscopic and magnetic measurements. As this distribution is more uniform than that generally attainable in commercial plating, the results of the exposure tests apply approximately to the *minimum* and not the average thicknesses of plating on commercial articles.

(a) NICKEL PLATING

The conditions used for the "standard" and "high sulfate" nickel baths are listed in table 4.

TABLE 4.—*Compositions and operating conditions of nickel baths*

COMPOSITION

	"Standard" nickel bath				"High-sulfate" nickel bath			
	N	*M*	*g/liter*	*oz/gal*	*N*	*M*	*g/liter*	*oz/gal*
Nickel sulfate, $NiSO_4.7H_2O$	1.4		200	27	0.5		75	10
Nickel chloride, $NiCl_2.6H_2O$	.4		45	6				
Ammonium chloride, NH_4Cl					.25		15	2
Sodium sulfate, Na_2SO_4					1.5		110	15
Boric acid, H_3BO_3		0.5	30	4		0.25	15	2

OPERATING CONDITIONS

Type of operation	pH	Temperature		Current density		pH	Temperature		Current density	
		°C	°F	amp/dm²	amp/ft²		°C	°F	amp/dm²	amp/ft²
Standard	5.3	35	95	2	19	5.5	22	72	1.3	12
With air agitation	5.3	50	122	4	37	5.5				
With low pH	2.5	60	140	4	37	5.5				
Over Cu deposit	5.3	40	104	4	37	5.5				
Over high-sulfate Ni	5.3	40	104	5	48	5.5				
Strike (45 seconds)	5.3					5.5	22	72	4.5	42

In 1938, specimens were plated at the National Bureau of Standards from four proprietary "bright nickel" baths. The compositions of the baths were undisclosed, but the plating was done under the supervision of representatives of the companies that supplied the baths. The specimens from the four baths were mixed and were exposed and inspected without identification. The results for bright nickel therefore represent a composite of the four types used.

In 1938 several sets of zinc-base die-castings were plated in proprietary bright nickel baths in three commercial plating plants. The specimens from the three plants were mixed, exposed, and inspected without identification.

(b) COPPER PLATING

The acid copper bath and the two cyanide copper baths are described in tables 5 and 6.

TABLE 5.—*Composition and operating conditions of acid copper-plating bath*

Composition					Temperature		Current density	
	N	*g/liter*	*oz/gal*	*fl oz/gal*	°C	°F	amp/dm²	amp/ft²
Copper sulfate, $CuSO_4.5H_2O$	2	250	33		35	95	2.5	23
Sulfuric acid, H_2SO_4	1.5	75	10	5.7	35	95	2.5	23

TABLE 6.—*Composition and operating conditions of cyanide copper-plating baths*

COMPOSITION

	"Standard" cyanide (used in 1936)			"Rochelle salt" (used in 1938)		
	N	*g/liter*	*oz/gal*	*N*	*g/liter*	*oz/gal*
Copper cyanide, CuCN	0.25	23	3	0.33	30	4
Total sodium cyanide, NaCN	.65	34	4.5	.75	38	5
Free sodium cyanide, NaCN	.15	7.5	1	.09	4.5	.6
Sodium carbonate, Na_2CO_3	.30	15	2	.60	30	4
Rochelle salt, $NaKC_4H_4O_6.4H_2O$				.32	45	6

OPERATING CONDITIONS

pH (glass electrode, uncorrected)			11.5
Temperature	°C	50	65
	°F	122	149
Current density	amp/dm²	1.5	3
	amp/ft²	14	28

(c) CHROMIUM PLATING

The conditions used in chromium plating are listed in table 7.

TABLE 7.—*Composition and operating conditions of chromium-plating bath*

COMPOSITION

	M	*N*	*g/liter*	*avdp oz/gal*	*fl oz/gal*
Chromic acid, CrO_3	2.5		250	33	
Sulfuric acid, H_2SO_4		0.05	2.5	.33	0.19

OPERATING CONDITIONS

Type of operation	Temperature		Current density	
	°C	*°F*	*amp/dm²*	*amp/ft²*
On brass or nickel	45	113	16	150
Directly on zinc, "warm"	45	113	18	170
Directly on zinc, "cold"	30	86	10	93

4. BUFFING

All of the plain nickel coatings and about half of the bright nickel coatings were "colored" on "loose buff" cloth wheels with commercial buffing compounds. A few of the copper coatings (indicated in the tables) were also buffed. The direct chromium coatings were "colored" on a sewed buff and were finished on a loose buff. The loss in weight by buffing (usually 5 to 10 percent of the coating) was determined in trial runs, and was taken into account, so that the buffed deposits had the specified thicknesses (within ±5 percent).

5. SCHEDULE OF DEPOSITS

The compositions and thicknesses of the deposits are listed in tables 8, 9, and 10. The specimens comprising those sets with no letter following the serial designation number were plated and exposed in 1936, and those with such a letter were plated and exposed in 1938. Many of the latter sets duplicated earlier ones. In these tables and throughout the text, the term "standard," as applied to a bath or deposit, merely designates a basis for comparison and is not an evidence of superiority.

TABLE 8.—*Plated coatings on steel and iron*

Set	Basis metal	Coating					Variations
		Composition	Thickness				
			Ni	Cu	Ni	Cr	
			in.	*in.*	*in.*	*in.*	
S 1	Cold-rolled steel I.	Ni	0.001				Standard Ni.
S 101	do	Ni, Cr	.001			0.00002	Standard Ni, Cr.
S 101A	do	do	.001			.00002	Cathode pickle.
S 102	do	do	.002			.00002	Thickness of Ni.
S 106	do	Cu(Cy), Ni, Cr		0.0005	0.0005	.00002	Cu layer.
S 109A	do	do		.0005	.0005	.00002	Bright Ni.
S 109B	do	Ni, Cu(Ac), Ni, Cr	.0002	.0003	.0005	.00002	Acid-Cu layer.
S 113	do	Ni, Cu(Cy), Ni, Cr	.0002	.0003	.0005	.00002	Cyanide-Cu layer.
S 114	do	Ni, Cu(Ac), Ni, Cr	.0004	.0006	.001	.00002	Acid-Cu thickness.
S 116	do	Ni, Cu(Cy), Ni, Cr	.0002	.0005	.0003	.00002	Final Ni thin.
S 171	do	Ni, Cr	.001			.00005	Thickness of Cr.
S 172	do	do	.001			.0001	Do.
S 173	do	do	.002			.0001	Do.
S 174	do	do	.001			.00002	Air-agitated Ni bath.
S 175	do	do	.001			.00002	Different steel.
S 181	Cold-rolled steel II.	do	.001			.00002	Cathode pickle.
S 181A	do	do	.001			.00002	Cu layer.
S 182	do	Cu(Cy), Ni, Cr		.0005	.0005	.00002	Bright Ni.
S 189A	do	do		.0005	.0005	.00002	Different steel.
S 189B	do	Ni, Cr	.001			.00002	Cyanide-Cu layer.
S 191	Spring steel III.	Ni, Cu(Cy), Ni, Cr	.0002	.0003	.0005	.00002	Cu flash.
S 192	do	Cu[a](Cy), Ni, Cr		.00005	.002	.00002	Thick Cu.
I 1	Gray cast iron IV.	do.[a]		.001	.001	.00002	Thick Cu.
I 2	do	do.[a]		.00005	.002	.00002	Cu flash.
I 3	Malleable cast iron V.	do.[a]		.001	.001	.00002	Thick Cu.
I 4	do						

[a] These copper coatings were buffed.

TABLE 9.—*Plated Coatings on Copper and Brass*

Set	Basis metal	Costing				Variations
		Composition	Thickness			
			Cu	Ni	Cr	
			in.	*in.*	*in.*	
C 1	Copper, VI	Ni, Cr		0.0002	0.00002	Standard.
C 2	do	do		.0005	.00002	Thickness of Ni.
C 3	do	do		.0005	.00002	Citrate anodic etch.
C 4	do	Cr[a]			.0002	Direct Cr.
B 1	Cast high-brass VII	Ni, Cr		.0002	.00002	Standard.
B 2	do	do		.0001	.00002	Thickness of Ni.
B 3	do	do		.0005	.00002	Do.
B 4	do	do		.0002	.00001	Thickness of Cr.
B 5	do	Cu(Cy), Ni, Cr	0.00005	.0002	.00002	Cu flash.
B 6	do	Ni, Cr		.0002	.00002	H_2SO_4 anodic etch.
B 7	do	Cr[a]			.0002	Direct Cr.
B 11	Cast low brass VIII	Ni, Cr		.0002	.00002	Standard.
B 13	do	Cu(Cy), Ni, Cr	.00005	.0002	.00002	Cu flash.
B 14	do	Cr[a]			.0002	Direct Cr.
B 21	Extruded brass IX	Ni, Cr		.0002	.00002	Standard.
B 23	do	Cu(Cy), Ni, Cr	.00005	.0002	.00002	Cu flash.
B 24	do	Cr[a]			.0002	Direct Cr.
B 31	Rolled high-brass X	Ni, Cr		.0002	.00002	Standard.
B 31A	do	do		.0002	.00002	Bright Ni.
B 31B	do	do		.0002	.00002	No organic degreaser.
B 31C	do	do		.0002	.00002	Thickness of Ni.
B 32	do	do		.0001	.00002	
B 32A	do	do		.0002	.00008	Thickness of Cr.
B 33	do	do				
B 33A	do	do		.0005	.00002	Thickness of Ni.
B 34	do	do				
B 34A	do	do				

[a] These Cr layers were buffed.

TABLE 9.—*Plated Coatings on Copper and Brass*—Continued

Set	Basis metal	Coating				Variations
		Composition	Thickness			
			Cu	Ni	Cr	
			in.	*in.*	*in.*	
B 34B	Rolled high-brass X	Ni, Cr		0.0005	0.00002	Bright Ni.
B 35	do	do		.0002	.00001	Thickness of Cr.
B 35A						
B 36	do	do		.0003	.00002	Thickness of Ni.
B 36A						
B 37	Rolled high brass X	do		.0002	.00005	Thickness of Cr.
B 37A						
B 38	do	Ni		.0002		No chromium.
B 38A						
B 39	do	Cr			.00003	Direct Cr, thin.
B 40	do	Cu(Cy), Ni, Cr	0.00005	.0002	.00002	Cyanide-Cu flash.
B 41	do	Cu(Ac), Ni, Cr	.00005	.0002	.00002	Acid-Cu flash.
B 42	do	Ni, Cr		.0002	.00002	Nickel, not buffed.
B 43	do	do		.0002	.00002	Citrate anodic etch.
B 44	do	Cr*			.0002	Direct Cr, thick.
B 45	do	Ni, Cr		.0002	.00002	H_2SO_4 anodic etch.
B 46	do	do		.0002	.00002	Low pH Ni.
B 47	do	do		.00005	.00002	Thickness of Ni.
B 47A						
B 48	do	do		.0002	.00002	Air-agitated Ni bath.
B 51	Rolled low brass XI	do		.0002	.00002	Standard.
B 53	do	Cr*			.0002	Direct Cr.
B 54	do	Ni, Cr		.0002	.00002	H_2SO_4 anodic etch.
B 55	do	do		.0002	.00002	H_2SO_4 anodic etch; low pH, Ni
B 56A	Rolled high brass X	do		.00015	.00002	Thickness of Ni.
B 57A	do	do		.001	.00002	Do.
B 8A	do	do		.0002	.000005	Thickness of Cr.
B 59A	do	do		.0002	.00002	Brass bright-dipped.
N 1	Rolled Ni brass XII	Cr*			.0002	Direct Cr.
N 2	do	Cr			.0001	Thickness of Cr.
N 3	do	do			.00005	Do.
N 4	do	Ni, Cr		.0001	.0001	Thickness of Ni, Cr.
N 5	do	do		.0002	.00002	Standard.
N 11	Cast Ni brass XIII	Cr*			.0002	Direct Cr.
N 12	do	do.*			.0001	Thickness of Cr.
N 13	do	do.*			.00005	Do.
N 14	do	Cu(Cy), Ni, Cr	.00005	.0002	.00002	Copper flash.
N 15	do	Ni, Cr		.0002	.00002	Standard.

* These chromium layers were buffed.

TABLE 10.—*Plated coatings on zinc and zinc-base die castings*

H, high sulfate nickel bath: S, standard nickel bath

Set	Basis metal	Coatings				Variations
		Composition	Thickness			
			Cu	Ni	Cr	
			in.	*in.*	*in.*	
Z 1	Rolled zinc XIV	Ni(HS), Cr		0.0005	0.00002	Standard.
Z 2	do	do		.0003	.00002	Thickness of Ni.
Z 3	do	do		.0005	.00003	Thickness of Cr.
Z 4	do	do		.0005	.00001	Do.
Z 5	do	Ni(HS), Ni(S), Cr		.0002 .0003	.00002	Duplex Ni.
Z 6	do	Cu(Cy), Ni(S), Cr	0.0002	.0003	.00002	Cu layer.
Z 11	Zinc alloy XXI	Ni(HS), Cr		.0005	.00002	Standard.
Z 12	do	Ni(HS), Ni(S), Cr		.0002 .0003	.00002	Duplex Ni.
Z 13	do	do		.0002 .0003	.00002	Thickness of Ni.
Z 14	do	Cu(Cy), Ni(S), Cr	.0002	.0003	.00002	Cu layer.
Z 15	do	do	.0001	.00009	.00002	Thickness of Cu, Ni.
Z 16	do	Cr*			.0001	Direct Cr, cold.
Z 17	do	Ni(HS), Cr		.001	.00002	Thickness of Ni.
Z 19	Zinc alloy XXIII	Ni(HS)		.0005		Standard Ni.
Z 20	do	do		.0003		Thickness of Ni.

* These Cr and Cu layers were buffed.

TABLE 10.—*Plated coatings on zinc and zinc-base die castings*—Continued

Set	Basis metal	Coatings				Variations
		Composition	Thickness			
			Cu	Ni	Cr	
			in.	*in.*	*in.*	
Z 22	Zinc alloy XXIII	Ni(HS), Cr		0.0005	0.00002	Standard Ni, Cr.
Z 22A						
Z 24	do	do		.0003	.00002	Thickness of Ni.
Z 24A						
Z 25	do	do		.0005	.00001	Thickness of Cr.
Z 26	do	do		.0005	.00003	Do.
Z 31	do	Cr[a]			.0001	Direct Cr.
Z 33	do	do[a]			.0001	Direct Cr, cold.
Z 35	do	Ni(HS), Ni(S), Cr		.0002 .0003	.00002	Standard duplex Ni.
Z 35A						
Z 36	do	do		.0002 .0003	.00001	Thickness of Cr.
Z 37	do	do		.0002 .0008	.00002	Thickness of Ni.
Z 37A						
Z 38	do	do		.0002 .0018	.00002	Do.
Z 38A						
Z 40	do	Cu(Cy), Ni(S), Cr	0.0002	.0003	.00002	Standard Cu, Ni, Cr.
Z 40A						
Z 41	do	do	.0004	.0006	.00002	Thickness of Cu, Ni.
Z 41A						
Z 42	do	Cu[a](Cy), Ni(S), Cr	.0005	.0015	.00002	Do.
Z 42A						
Z 43	do	Cu(Cy), Ni(S), Cr	.0003	.0002	.00002	Ratio Cu/Ni.
Z 45	do	Ni(HS), Cu(Cy), Ni (S), Cr.	.0003	.0002 .0005	.00002	Intermediate Cu layer.
Z 47	do	Ni(HS), Cr		.001	.00002	Thickness of Ni.
Z 48	do	do		.0002	.00002	Do.
Z 48A						
Z 49	do	Cu[a](Cy), Ni(S), Cr	.0005	.00075	.00002	Thickness of Cu, Ni.
Z 50	do	Cu[a](Cy), Cr	.0005		.00002	No Ni.
Z 51A	do	Ni(HS), Cr		.00075	.0002	Thickness of Ni.
Z 52A	do	Ni(HS), Ni(S), Cr		.0003 .00075	.00002	Standard duplex Ni.
Z 53A	do	Cu(Cy), Ni(S), Cr	.00025	.0005	.00002	Standard Cu, Ni.
Z 53B	do	Cu(Cy), Ni(B), Cr	.00025	.0005	.00002	Bright Ni.
Z 53E,G,H	do	do	.00025	.0005	.00002	Bright Ni in commercial plants.
Z 54A	do	Cu(Cy), Ni(S), Cr	.00025	.0005	.00001	Thickness of Cr.
Z 55A	do	do	.00025	.0005	.00003	Do.
Z 56A	do	do	.00025	.0005	.00005	Do.
Z 61A	Zinc alloy XXI	do	.00025	.0005	.00002	Different Zn alloy.
Z 61B	do	Cu(Cy), Ni(B), Cr	.00025	.0005	.00002	Bright Ni.
Z 61E,G,H	do	do	.00025	.0005	.00002	Bright Ni in commercial plants.

[a] These Cr and Cu layers were buffed.

III. ATMOSPHERIC EXPOSURE TESTS

1. CONDITIONS OF EXPOSURE

Five specimens of each set were exposed in each of six locations: Key West, Fla.; New York, N. Y.; Pittsburgh, Pa.; Sandy Hook, N. J.; State College, Pa.; and Washington, D. C. The racks were located as described in NBS Research Paper RP712, page 336, except that in Pittsburgh in 1938 the new specimens were exposed on the roof of a Bureau of Mines' Building. Although the atmosphere there is somewhat less contaminated than at the former location on Brunot's Island, it still represents a severe industrial exposure. The racks and mounting were the same as in the previous exposure tests (Research Papers RP712 and RP867).

2. METHOD OF INSPECTION AND RATING

In the previous exposure tests, each inspector assigned to each specimen a numerical rating from 0 to 5, based upon the percentage of the surface that was rusted. In the tests here described, this scale was applied to coatings on nonferrous metals, taking into account *all* evidences of failure, such as light or dark stains, blisters, cracks, and peeling, to each of which equal weight was given.

The ratings of the steel specimens exposed in 1936 were based upon rust only and were therefore directly comparable with those reported in previous papers. In order to make the ratings of coatings on steel also comparable with those on the nonferrous metals, in the 1938 exposures the steel specimens were rated separately for (a) rust and (b) all defects including rust. The results obtained by the two methods of rating were nearly alike, which indicates that in 1938 the rusting was the predominating cause of failure. In some of the earlier tests on steel, when a greater variety of coatings was included, considerable blistering and peeling were observed, which were reported but were not taken into account in the numerical ratings and scores.

The scores were obtained by multiplying the average rating during each inspection period by the number of weeks in that period. The "total scores" were then converted to "percentage scores"; that is, to the percentage of a perfect score for the total period of exposure involved. In this system the results in different locations are directly comparable, even though the periods of exposure may not be identical. The relation of these numerical values is given in table 11, which shows that this scale is not a linear, but a roughly logarithmic function of the proportion of the surface that is corroded.

TABLE 11.—*System used for rating of the specimens*

Proportion of surface with rust or other defects		Rating	Corresponding score	Proportion of surface with rust or other defects		Rating	Corresponding score
Range	Average			Range	Average		
%	%		%	%	%		%
0		5	100	10 to 20	15	2	40
0 to 5	2.5	4	80	20 to 50	35	1	20
5 to 10	7.5	3	60	50 to 100	75	0	0

During the last series of exposures, E. M. Baker[7] suggested that, in addition to the numerical ratings, each inspector should indicate whether, in his opinion, the specimens were still "satisfactory" as judged from the standpoint of a user. Such a system might permit a decision as to how long a certain coating would give good service under the prevailing conditions. In effect, it gives each inspector an opportunity to weight the different types of failure according to his opinion, instead of giving equal weight to all kinds of failure.

It was possible to apply this supplemental rating at only two inspection periods, and after many of the specimens had obviously failed. Therefore the data obtained are not valid evidence of the

[7] University of Michigan. Private communication.

possible value of the method if it had been applied throughout the exposures. Most inspectors reported as "unsatisfactory" those specimens with a rating of 3 or less. In a few cases, specimens with a rating of 4, but with a single conspicuous defect, were also reported as "unsatisfactory." These few observations indicate that the numerical system of rating yields a good measure of quality, although it may not record minor differences. In any similar future tests, Baker's plan may well be given a more thorough trial as a supplement to the numerical ratings.

Exposure tests of plated coatings in one or more locations cannot be expected to yield absolute figures for the protective value of various coatings in service, as service conditions may involve various factors that are either not present, or are not present in the same degree in the exposure tests. The exposure data are useful chiefly for indicating the relative value of various coatings, and especially their order of merit.

In interpreting the data it is necessary to estimate their reproducibility; that is, the magnitude of differences that are likely to be significant. Analysis of the thousands of ratings made by different inspectors at different locations and at various periods indicates that the five specimens of each set were very uniform in behavior. It was very unusual for one specimen to differ by more than one point from the others of that set, that is, to influence the average by more than about 0.2 point. The ratings of any one of three or more inspectors for a set seldom differed from their average by more than one point. The averages were probably reliable to 0.5 point, which is 10 percent on the scale. In a series of inspections, any tendency for one person or group to mark high or low would not affect the relative scores of the sets at that location, although it might influence the comparative values at different locations. From all considerations, it is believed that the final percentage scores are consistent within ± 10 percent. Therefore no major conclusions have been based on differences of less than 10 percent from the average, although consistent smaller differences may be valid evidence of trends in the results.

In tables 12 to 24 are recorded the percentage scores of each set in each location and the average for each set in the six locations. For groups of comparable coatings, for example those with the same thickness but differing in the basis metal or method of application, the average scores have also been computed. Each score that differs by more than 10 percent from the average of comparable scores is marked with an "a". The average deviation from the mean value for each group is indicated after each mean, for example 54 ± 5 percent. The fact that most of these average deviations are less than 10 percent shows that the effects of many of the variables studied were less than the reproducibility of the observations.

3. USE OF COLOR PHOTOGRAPHY

Although the numerical system of rating yields very useful comparisons of the coatings, it does not furnish a permanent objective record of their appearance at any given inspection. In an effort to

obtain such a record, color photographs were made of many of the specimens in the different locations.[8] The results showed that although color photographs are much more informative than black and white pictures, they do not record the same appearance that is seen by the eye. It was especially difficult to obtain authentic pictures of mirror surfaces, which reflected the sky or other surrounding surfaces. The results to date may be considered as purely exploratory, but they are sufficiently promising to warrant a thorough study in any future tests, including means of securing more uniform illumination.

4. EFFECT OF CLEANING THE EXPOSED SPECIMENS

The scores listed in the tables are based on the appearance of the specimens during continuous exposure, with no treatment except light brushing to remove loose dust. Especially in New York and Pittsburgh, sufficient dust and soot adhered to the specimens to prevent accurate estimates of the extent of corrosion or tarnish. In some locations the corrosion products spread over the surface and gave misleading results.

To determine the true condition of the surfaces, one specimen of each set was cleaned with water and fine tripoli after 1 year's exposure. In the four severe exposure sites (Key West, New York, Pittsburgh, and Sandy Hook), the cleaning improved the ratings on iron and steel by about one point, for example from a rating of 2 to a rating of 3, on copper and brass by about two points (somewhat more on nickel-brass), and on zinc by about one point. These results show that on exposure the plated brass is less deeply corroded than is the steel or zinc. Within a few months the cleaned specimens had about the same ratings as those not cleaned. The cleaning should therefore be considered merely as an aid to inspection and not as a preventive of failure. At best, it is difficult to apply any cleaning procedure uniformly, especially by different persons in various locations and at different seasons, and hence cleaning was not included in the regular inspections.

5. EFFECT OF A GREASE FILM APPLIED TO THE COATINGS

The widespread and generally beneficial use of a grease or wax film on plated parts of automobiles might lead one to consider such a treatment as a panacea for defective plating. To throw light on this question, one or two specimens of each set were given a thin film of petrolatum by brushing the surface with a 2-percent solution of petrolatum in mineral spirits. (Prior to use, both materials were tested by standard methods and found to cause no tarnishing of copper.) As the resultant thin grease film (about 0.000005 in.) tended to hold dust, the surface was wiped with a dry cloth prior to each inspection, and a new film of grease was applied after the inspection.

The results showed that, in general, the ratings of the greased specimens were about one to two points higher than those of the ungreased, that is, 10 to 20 percent less of the surface had failed.

[8] C. A. Vincent-Daviss and W. Blum, *The use of color photography for recording the results of exposure tests*, Monthly Rev. Am. Electroplaters' Soc. **24**, 818 (1937).

The sets were usually in the same order; that is, specimens with inferior coatings (for example, with no nickel under the chromium) failed most rapidly, whether greased or not. However, in a few sets, especially in marine locations, the greased specimens failed more rapidly than those without grease. It is possible that any salt absorbed by the dust on the greased specimens was not as readily removed by rain as the salt on the other specimens.

The petrolatum solution was used because it produced a transparent film of fairly uniform thickness and entered the pores. A suitable wax mixture might have yielded better or more prolonged protection, but it would have been more difficult to apply uniformly.

Although a grease or wax film is generally advantageous, it does not justify the use of thin or porous coatings. Especially in marine locations, it should be frequently removed and renewed.

IV. EFFECTS OF ATMOSPHERIC EXPOSURE

1. EFFECT OF ENVIRONMENT

Of the six locations, State College and Washington may be considered as mild exposures, Key West and Sandy Hook as marine, and New York and Pittsburgh as industrial. In the mild locations only those sets that were very poor elsewhere showed marked failure, but most of the others had scores of 90 percent or more even after 2 years of exposure. In the following tables, data are included for each location. The principal conclusions are based on the average of the six locations, which represents, at least roughly, an average condition of outdoor exposure, such as miscellaneous plated articles might be required to withstand. For certain coatings, or for special purposes, the data for a particular type of exposure may be of more interest than the average of all locations.

2. PROTECTIVE VALUE OF COATINGS

The following conclusions are based principally upon exposures of the 1936 specimens for 2.2 years (except in Pittsburgh, where practically all of the specimens had failed within 1 year), and of the 1938 specimens for 1.3 years.

(a) ON STEEL

The data obtained with coatings on steel are summarized in tables 12 and 13, from which the following conclusions are drawn regarding effects of the specified variables.

(1) *Effect of thickness of nickel (plus copper).*—As only two total thicknesses (0.001 and 0.002 in.) were included, their average results (54 and 77 percent) merely confirm the increase in protective value with thickness of coating that was reported in Research Paper RP712.

TABLE 12.—*Effect of variations in thickness of nickel (plus copper) on steel and iron*

TABLE 12.—*Effect of variations in thickness of nickel (plus copper) on steel and iron*

[Unless otherwise noted, Cr=0.00002 in. Tests started in 1936; total time 2.2 years (except for P only 1 year). Based on rust only.]

Set	Basis metal	Variation	*T* equals total percentage score													
			KW		NY		P		SH		SC		W		General average	
			T	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg
			(a) 0.001 in. total Cu+Ni													
			%	%	%	%	%	%	%	%	%	%	%	%	%	%
S 1	Cold-rolled I	No Cr	57	+8	38	0	38	•+11	39	•+12	72	•−21	81	−6	54	−0
S 101	do	Standard	51	+2	48	+10	18	−9	29	+2	85	−8	84	−3	53	−1
S 102	do	Cathode pickle	43	−6	41	+3	32	+5	34	+7	90	−3	79	−8	53	−1
S 113	do	Ni, Cu(A), Ni	31	•−18	31	−7	17	−10	13	•−14	98	+5	88	+1	46	−8
S 114	do	Ni, Cu(CN), Ni	45	−4	26	•−12	17	−10	18	−9	99	+6	96	+9	50	−4
S 171	do	Final Ni thin	34	•−15	26	•−12	17	−10	15	•−12	94	+1	87	0	46	−8
S 175	do	Ni-air agitation	46	−3	46	+8	35	+8	26	−1	94	+1	82	−5	55	+1
S 181	Cold-rolled II	Standard	70	•+21	48	+10	34	+7	45	•+18	100	+7	92	+5	65	•+11
S 182	do	Cathode pickle	65	•+16	46	+8	34	+7	30	+3	100	+7	90	+3	61	+7
S 191	Spring steel	Standard	64	•+15	36	−2	42	•+15	27	0	94	+1	83	−4	58	+4
S 192	do	Ni, Cu(CN), Ni	35	•−14	29	−9	17	−10	18	−9	97	+4	93	+6	48	−6
		Average	49	±10	38	±7	27	±9	27	±8	93	±6	87	±5	54	±5
S 172 [b]	Cold-rolled I	0.00005 in. of Cr	70	.....	61	.....	58	.....	67	.....	96	.....	82	.....	72	.....
S 173 [b]	do	.0001 in. of Cr	79	.....	67	.....	51	.....	68	.....	89	.....	87	.....	74	.....
			(b) 0.002 in. total Cu+Ni													
S 106	Cold-rolled I	Standard	84	+9	75	•+22	64	+5	66	−8	100	+1	99	+1	81	+4
S 116	do	Ni, Cu(A), Ni	84	+9	47	−5	44	•−15	77	+3	100	+1	99	+1	75	−2
S 174	do	0.0001 Cr	81	+6	69	•+16	52	−7	79	+5	100	+1	96	−2	80	+3
I 1	Gray cast	Cu(flash), Ni	77	+2	49	−4	67	+8	75	+1	99	0	98	0	78	+1
I 2	do	Cu(CN), Ni	79	+4	40	•−13	62	+3	77	+3	99	0	98	0	76	−1
I 3	Malleable	Cu(flash), Ni	52	•−23	53	0	67	+8	73	−1	98	−1	98	0	74	−3
I 4	do	Cu(CN), Ni	70	−5	35	•−18	57	−2	72	−2	99	0	99	+1	72	−5
		Average	75	±8	53	±11	59	±7	74	±3	99	±1	98	±1	77	±3

• Sets differing by more than 10 percent from average of comparable sets.

[b] Not included in average.

TABLE 13.—*Comparison of bright and plain nickel on steel*

[Test started in 1938; 1.3 years of exposure. All coatings (except 101A and 181A, which are 0.001 in. Ni, plus 0.00002 in. Cr) have 0.0005 in. Cu, 0.0005 in. Ni, and 0.00002 in. Cr. Based on all defects.]

Set	Steel	Nickel	*T* equals total percentage scores																	
			KW		NY		P		SH		SC		W		General average	
			T	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg
			%	%	%	%	%	%	%	%	%	%	%	%	%	%
S 109A	Reg. I	Plain	40	*−20	25	−8	24	−8	19	−8	88	−3	80	+3	46	−8
S 109B	do	Bright, not buffed	64	+4	37	+4	30	−2	42	*+15	98	+7	79	+2	60	+6
S 109B	do	Bright, buffed	60	0	37	+4	37	+6	31	+4	89	+2	78	−1	55	+1
S 180A	Spec. II	Plain	47	*−13	26	−7	22	−10	21	+6	89	+2	79	+2	48	−6
S 180B	do	Bright, not buffed	57	−3	31	−2	38	+6	34	+7	96	+5	70	−7	54	0
S 180B	do	Bright, buffed	66	+6	34	+1	32	0	27	0	88	−3	76	−1	56	+2
S 101A	Reg. I	Plain	71	*+11	44	*+11	45	*+13	24	−3	83	−8	76	−1	57	+3
S 181A	Spec. II	do	72	*+12	32	−1	33	+1	19	−8	96	+5	80	+3	55	+1
		Average	60	±9	33	±5	32	±6	27	±6	91	±4	77	±3	54	±3

* Sets differing by more than 10 percent from average of comparable sets.

(2) *Effect of preparation for plating.*—No significant effect on protective value was produced by cathodic pickling (S102 and S182) upon the extent of rust, but observations not included in the tables show that there was more tendency for the formation of small blisters in the coatings on the cathodically pickled steel.

(3) *Effect of method of nickel plating; (a) Air agitation.*—The use of air agitation (S 175) in the nickel bath had no significant effect.

(*b*) *Bright nickel.*—The proprietary *"bright nickel"* deposits (table 13) yielded, on the average, at least as much protection as plain nickel, but showed slightly more tendency to crack. On all three types of basis metal there was much more variation in the quality of the bright nickel than of the buffed plain nickel coatings. Evidently some of the bright nickel deposits were superior and others were inferior to comparable plain nickel deposits. As the different bright nickel coatings were not identified, only their average performance can be reported. (These and other comparisons of bright nickel in this paper refer only to the coatings from the four solutions used in 1938 for this investigation, in which improvements may since have been made.)

(4) *Effect of a copper layer.*—The data in table 12 indicate that in four sets (S 113, S 114, S 171, and S 192) with a total thickness of 0.001 in., the presence of a copper layer consistently gave scores slightly (7 percent) below the average. This effect was less evident with the 0.002-in. coatings. This result is consistent with those reported in RP712, and indicates that even in relatively thick deposits on steel a copper layer does not have a protective value equal to that of the same thickness of nickel.

(5) *Effect of thickness of chromium.*—The results in table 12 with sets S 172 and S 173 show that a greater thickness of chromium than the customary 0.00002 in. adds materially to the protection against corrosion, as was reported in RP712. Some cracking of these thick chromium coatings occurred, but not nearly so much as with thick chromium coatings over nickel on brass.

(6) *Effect of the basis metal.*—In general (table 12), about the same protection was afforded by a coating 0.002 in. thick on cold-rolled steel, spring steel, gray cast iron, and malleable cast iron.

The data for cold-rolled steels I and II in table 12 show that the latter, which was "full cold-rolled" or "satin finish" steel, was about 10 percent superior to the average (compare S 101 and S 181). In addition, steel II showed somewhat less tendency to blister on the specimens cathodically pickled (S 102 and S 182). However, no such differences in these two steels were observed (table 12) in 16 months' exposure of 1938 specimens (S 101A and S 181A). These few results indicate that variations in a given type or finish of steel may be as significant as variations of type.

(b) ON COPPER AND BRASS

The data in tables 14 to 19 for coatings on copper and brass lead to the following conclusions.

TABLE 14.—*Effect of variations in thickness of nickel (plus copper) on copper, brass, and nickel-brass*

[Scores for all defects. Unless otherwise noted, Cr 0.00002 in. Tests started in 1936; total time 2.2 years]

Set	Basis metal	Nickel thickness	Variation	*T* equals total percentage scores													
				KW		NY		P		SH		SC		W		General	
				T	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.
		in.	Direct Cr:	%	%	%	%	%	%	%	%	%	%	%	%	%	%
C 4	Cu	0	0.0002	19	−4	4	−1	12	0	6	−8	30	•−37	32	•−28	17	•−13
B 7	Cast high brass	0	.0002	14	−9	4	−1	12	0	6	−8	76	?+9	56	−4	28	−2
B 14	Cast low brass	0	.0002	18	−5	8	+3	12	0	14	0	95	•+28	86	•+26	39	+9
B 24	Extruded brass	0	.0002	21	−2	4	−1	12	0	11	−3	51	•−16	61	+1	27	−3
B 44	Rolled high brass	0	.0002	22	−1	4	−1	12	0	13	−1	61	−6	45	•−15	26	−4
B 53	Rolled low brass	0	.0002	21	−2	4	−1	12	0	10	−4	61	−6	33	•−27	24	−6
N 1	Rolled Ni brass	0	.0002	35	•+12	6	+1	12	0	28	•+14	72	+5	76	•+16	38	+8
N 11	Cast Ni brass	0	.0002	33	+10	4	−1	12	0	26	•+12	91	•+24	88	•+28	42	•+12
			Average	23	±6	5	±1	12	0	14	±6	67	±16	60	±18	30	±7
B 47[b]	Rolled high brass	0.00005	Thickness of Ni	54		15		17		29		89		69		46	
B 2	Cast high brass	.00010	do	43	−10	12	−7	16	−7	13	−9	89	−2	61	−10	39	−8
B 32	Rolled high brass	.00010	do	63	+10	26	+7	29	+6	31	+9	93	+2	80	+10	54	+7
			Average	53	±7	19	±7	23	±7	22	±9	91	±2	71	±10	47	±8
C 1	Cu	.00020	Standard	56	−1	25	+1	12	−9	34	+5	97	+3	94	+6	53	+1
B 1	Cast high brass	.00020	do	62	+5	23	−1	12	−9	23	−6	100	+6	79	−9	50	−2
B 6	do	.00020	Anodic, H_2SO_4	49	−8	33	+9	34	•+13	45	•+16	94	0	83	−5	56	+4
B 11	Cast low brass	.00020	Standard	63	+6	28	+4	38	•+17	27	−2	96	+2	83	−5	56	+4
B 21	Extruded brass	.00020	do	57	0	28	+4	20	−1	28	−1	94	0	91	+3	53	+1
B 31	Rolled high brass	.00020	do	68	•+11	18	−6	20	−1	20	−9	92	−2	71	•−17	48	−4
B 43	do	.00020	Anodic, citrate	53	−4	25	+1	21	0	30	+1	87	−7	95	+7	52	0
B 45	do	.00020	Anodic, H_2SO_4	57	0	21	−3	16	−5	28	−1	88	−6	91	+3	50	−2
B 46	do	.00020	Low pH Ni	57	0	21	−3	21	0	22	−7	90	−4	92	+4	51	−1
B 48	do	.00020	Air-agitated Ni	63	+6	25	+1	24	+3	34	+5	92	−2	94	+6	56	+4
B 51	Rolled low brass	.00020	Standard	53	−4	26	+2	18	−3	32	+3	96	+2	90	+2	53	+1
B 54	do	.00020	Anodic, H_2SO_4	55	−2	25	+1	12	−9	28	−1	97	+3	94	+6	52	0
B 55	do	.00020	Anodic, H_2SO_4; low pH Ni	55	−2	18	−6	21	0	32	+3	97	+3	95	+7	53	+1
N 5	Rolled Ni brass	.00020	Standard	51	−6	23	−1	18	−3	42	•+13	96	+2	95	+7	54	+2
N 15	Cast Ni brass	.00020	do	55	−2	23	−1	20	−1	18	−11	96	+2	97	+9	49	−3

N 5	Rolled Ni brass	.00020	Standard	51	−6	23	−1	18	−3	42	•+13	96	+2	95	+7	54	+2
N 15	Cast Ni brass	.00020	do	55	−2	22	−2	29	+8	18	−11	89	−5	77	−11	48	−4
			Average	57	±4	24	±3	21	±5	29	±6	94	±3	88	±7	52	±2
			Copper flash under nickel:														
B 5	Cast high brass	.00020	Cyanide Cu	46	−10	14	•−14	12	•−13	29	−5	92	−3	94	+7	48	−6
B 13	Cast low brass	.00020	do	39	•−17	29	+1	26	+1	24	−10	100	+5	81	−6	50	−4
B 23	Extruded brass	.00020	do	56	0	22	−6	20	−5	32	−2	88	−7	91	+4	52	−2
B 40	Rolled high brass	.00020	do	74	•+18	40	•+12	35	+10	43	+9	94	−1	94	+7	63	+9
B 41	do	.00020	Acid Cu	64	+8	42	•+14	37	•+12	40	+6	96	+1	95	+8	62	+8
N 14	Cast Ni brass	.00020	Cyanide Cu	57	+1	21	−7	21	−4	34	0	97	+2	65	•−22	49	−5
			Average	56	±9	28	±9	25	±8	34	±5	95	±3	87	±9	54	±6
B 36[b]	Rolled high brass	.00030	Standard	57		24		12		25		93		86		50	
C 2	Cu	.00050	do	62	−5	19	−7	12	•−18	32	−5	100	+2	99	+4	54	−5
C 3	do	.00050	Anodic, citrate	62	−5	19	−7	18	•−12	31	−6	99	+1	93	−2	54	−5
B 3	Cast high brass	.00050	Standard	66	+1	28	+2	55	•+25	36	+1	98	0	94	−1	63	+4
B 34	Rolled high brass	.00050	do	78	•+11	37	•+11	33	+3	49	•+12	96	−2	95	0	65	+6
			Average	67	±6	26	±7	30	±15	37	±6	98	±1	95	±5	59	±5

• Sets differing by more than 10 percent from average of comparable sets.
[b] Not included in average.

TABLE 15.—*Effect of variations in thickness of nickel (plus copper) on copper, brass, and nickel-brass*

[Scores for all defects. Unless otherwise noted, Cr=0.00002 in. Tests started in 1938; total time 1.3 years]

Set	Base metal	Thickness of nickel	Variation	*T* equals total percentage scores																	
				KW		NY		P		SH		SC		W		General average	
				T	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg
		in.		% 39	% ----	% 13	% ----	% 9	% ----	% 18	% ----	% 85	% ----	% 69	% ----	% 39	% ----
B 47A	Rolled high brass	0.00005	Thickness of Ni	69	----	15	----	10	----	36	----	96	----	81	----	51	----
B 32A	do	.00010	do	88	----	17	----	9	----	22	----	88	----	73	----	45	----
B 66A	do	.00015	do														
B 31A	Rolled high brass	.00020	Standard	84	•+18	23	+3	11	+1	26	−3	100	+6	73	−5	53	+3
B 31C	do	.00020	No degreaser	65	−1	20	0	11	+1	35	+4	99	+5	81	+3	52	+2
B 50A	do	.00020	Bright-dipped	50	•−17	16	−4	9	−1	29	0	84	−10	80	+2	45	−5
			Average	66	±12	20	±2	10	±1	29	±2	94	±7	78	±3	50	±3
B 36A	Rolled high brass	.00030	Standard	68	----	14	----	24	----	42	----	99	----	92	----	57	----
B 34A	do	.00050	do	76	----	27	----	28	----	34	----	97	----	94	----	63	----
B 67A	do	.00100	Thickness of Ni	89	----	58	----	34	----	66	----	93	----	92	----	72	----

• Sets differing by more than 10 percent from average of comparable sets.

TABLE 16.—*Effect of variations in thickness of chromium over 0.0002 in. of nickel on brass*

[Tests started in 1936, total time 2.2 years]

Set	Basis metal	Cr thickness	Percentage scores						
			KW	NY	P	SH	SC	W	General average
		in.	%	%	%	%	%	%	%
B38	Rolled high	0	35	5	12	15	87	72	38
B4	Cast high	.000010	48	31	12	30	100	94	53
B35	Rolled high	.000010	59	20	12	17	88	88	47
Misc	(Table 14)	.000020	57	24	21	29	94	88	52
B33	Rolled high	.000030	53	20	18	23	91	90	49
B37	do	.000050	40	10	16	18	59	38	30

TABLE 17.—*Effect of variations in thickness of chromium over 0.0002 in. of nickel on brass*

[Tests started in 1938; total time 1.3 years]

Set	Basis metal	Cr thickness	Percentage scores						
			KW	NY	P	SH	SC	W	General average
		in.	%	%	%	%	%	%	%
B38	Rolled high	0	34	14	9	25	98	62	40
B38A	do	.000005	46	9	9	13	93	87	43
B35A	do	.000010	69	15	16	28	93	89	52
B31A	do	.000020	84	23	11	26	100	73	53
B33A	do	.000030	76	58	31	65	99	73	67
B37A	do	.000050	36	10	10	12	79	58	34

TABLE 18.—*Effect of variations in thickness of chromium directly on nickel-brass*

[Tests started in 1936; total time 2.2 years]

Set	Basis metal	Cr thickness	*T* equals total percentage scores													
			KW		NY		P		SH		SC		W		General average	
			T	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg
		in.	%	%	%	%	%	%	%	%	%	%	%	%	%	%
N3	Rolled	0.00005	36	+1	8	+2	12	----	15	−9	52	*−27	66	−9	32	−6
N13	Cast	.00005	34	−1	6	0	12	----	24	0	90	*+11	74	−1	40	+2
N2	Rolled	.00010	41	+6	4	−2	12	----	25	+1	75	−4	58	*−17	36	−2
N12	Cast	.00010	32	−3	5	−1	12	----	24	0	91	*+12	85	+10	42	+4
N1	Rolled	.00020	35	0	6	0	12	----	28	+4	72	−7	76	+1	38	0
N11	Cast	.00020	33	−2	4	−2	12	----	26	+2	91	*+12	88	*+13	42	+4
		Average	35	±2	6	±1	12	----	24	±3	79	±12	75	±9	38	±3

* Sets differing by more than 10 percent from average of comparable sets.

TABLE 19.—*Effect of "bright nickel" on brass*

[Tests started in 1938, total time 1.3 years. All on rolled high brass. Cr=0.00002 in. thick]

Set	Nickel		Percentage scores						
	Type	Thickness	KW	NY	P	SH	SC	W	General average
		in.	%	%	%	%	%	%	%
B 31A	Plain	0.0002	84	23	11	26	100	73	53
B 31B	Bright	.0002	85	35	43	50	94	70	63
	Average		85	29	27	38	96	72	58
B 34A	Plain	0.0005	76	27	42	34	97	94	62
B 34B	Bright	.0005	84	36	48	52	98	84	67
	Average		80	32	45	43	98	89	65

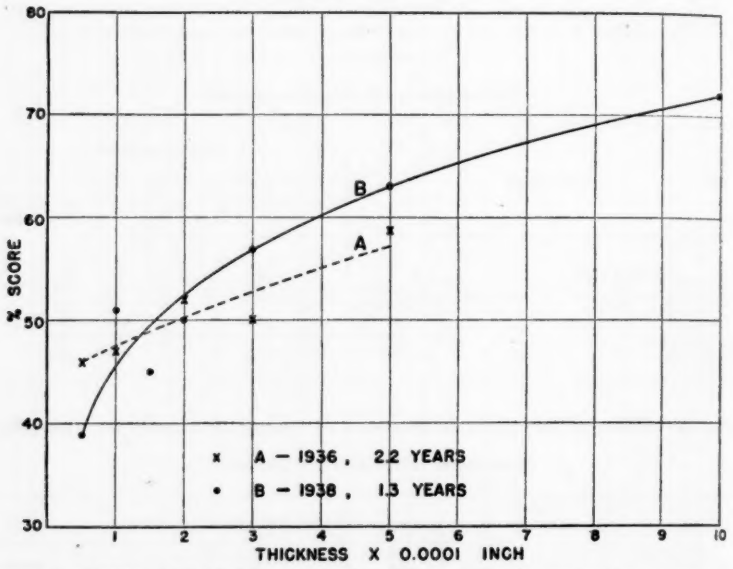

FIGURE 1.—*Effect of thickness of nickel on brass upon the percentage scores.*

Average of 6 locations. All nickel coatings covered with 0.00002 in. of chromium.

(1) *Effect of thickness of nickel.*—The scores for the first eight sets in table 14 show conclusively that when a relatively thick coating of chromium is applied directly to the copper or brass, with no intervening nickel, very little protection is furnished against corrosion, even in the mild locations. Nickel-brass (N 1 and N 11), which is often plated directly with chromium, behaves only slightly better than the other types of brass. Table 18 shows that the thickness of the chromium applied directly to nickel-brass has little effect.

Tables 14 and 15 show that as little as 0.00005 in. of nickel prior to the customary 0.00002 in. of chromium yields more protection than 0.0002 in. of chromium alone. The score increases as the thickness of nickel is increased but by no means proportionally to the latter. This is illustrated in figure 1 for all sets in the six locations for the 1936 and 1938 tests. (Because the scale is logarithmic, the actual reduction in

corrosion by an increase in thickness is greater than is indicated by the curves.) Although these and similar curves show clearly the general relation between thickness of nickel and protective value, they do not in themselves permit the selection of a certain thickness for a given purpose, which may involve factors other than atmospheric exposure.

(2) *Effect of preparation for plating.*—The data in table 14 show no effects of anodic etching of the brass upon the protective value of the coatings.

(3) *Effect of method of nickel plating*—(*a*) *Low pH.*—No significant effect was produced by the use of low pH nickel baths.

(b) *Agitation with air.*—No effect was produced by air agitation.

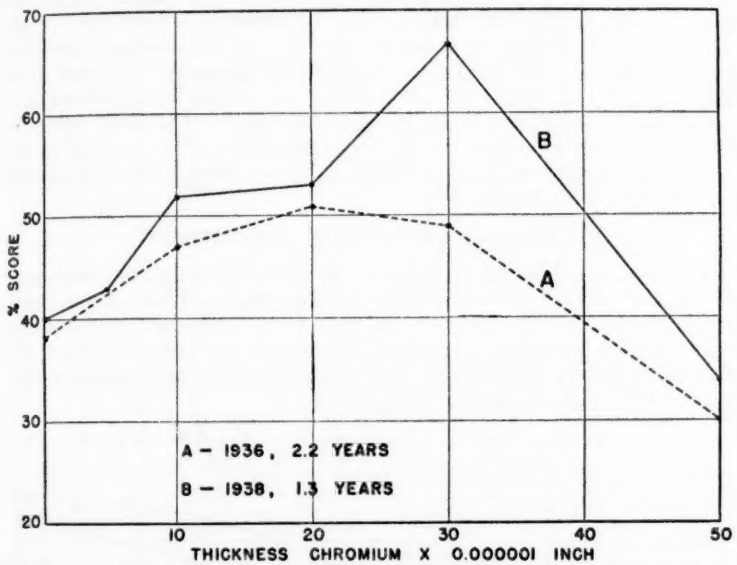

FIGURE 2.—*Effect of thickness of chromium over 0.0002 in. of nickel on brass upon the percentage scores.*

Average of 6 locations.

(c) *Bright nickel.*—The data in table 19 indicate that the bright nickel gave at least as much protection as plain nickel coatings. There was a tendency for the bright nickel on brass to crack but not so much as with the thicker bright nickel coatings on steel and on zinc.

(4) *Effect of a copper layer* (*table 14*).—The application of a "flash" (less than 0.00005 in.) of copper to brass prior to nickel plating bad no appreciable effect except on rolled high brass, where it produced an improvement of about 10 percent.

(5) *Effect of thickness of chromium.*—The data in tables 16 and 17 and in figure 2 show that as the thickness of chromium plated over 0.0002 in. of nickel on brass is increased, a maximum score is reached, after which there is a decided decrease in protection. The thickest chromium coatings (0.00005 in.) in both series of tests and in all locations showed pronounced cracking, which extended through the nickel and permitted corrosion of the brass.

Although it is not possible to select from these data the optimum thickness of chromium, which is apparently between 0.00001 and 0.00003 in., it is certain that 0.00005 in. of chromium is undesirable over the customary nickel coatings (0.0002 in.) on brass. The absence of severe cracking or corrosion with this thickness of chromium over 0.001 in. of nickel on steel (table 12), or over 0.00075 in. of nickel plus copper on zinc (table 23), may be caused by the fact that the cracking of the chromium could not extend through the greater thicknesses of copper and nickel.

(6) *Effect of the basis metal.*—The data in table 16 show surprisingly little difference in the behavior of similar coatings on copper and various kinds of brass, including even cast and rolled nickel-brass containing 18 percent of nickel. The nickel-brass specimens could be cleaned more readily and completely, that is, the tarnish and corrosion were more superficial than on regular brass or on steel or zinc. This fact and the nearly white color of the nickel-brass where it may be exposed by abrasion may justify the use of this alloy for certain purposes. As previously noted the application of a coating of nickel prior to the chromium is as valuable in preventing corrosion of nickel-brass as of regular brass.

(c) ON ZINC AND ZINC-BASE DIE CASTINGS

The data in tables 20 to 24 lead to the following conclusions:

(1) *Effect of thickness of nickel (plus copper).*—Chromium coatings plated directly on the zinc, that is, with no nickel layer, yielded almost no protection against corrosion. It required about 0.0003 in. of nickel to yield any appreciable protection, and the protection increased with the thickness as shown in figure 3.

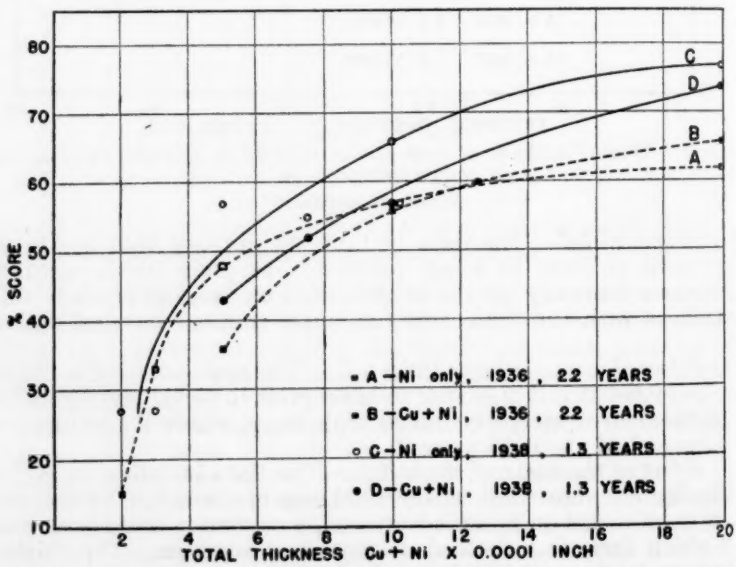

FIGURE 3.—*Effect of thickness of nickel, or of nickel plus copper, over zinc-base die-castings upon the percentage scores.*

Average of 6 locations. All nickel coatings covered with 0.00002 in. of chromium.

TABLE 20.—*Effect of variations in thickness of nickel (plus copper) on zinc and zinc die castings*

TABLE 20.—*Effect of variations in thickness of nickel (plus copper) on zinc and zinc die castings*

[HS, high sulfate nickel bath; S, standard nickel bath. Scores for all defects. Unless otherwise noted, Cr = 0.00002 in. Tests started in 1936; total time 2.2 years]

Set	Basis metal	Thickness Ni (+Cu)	Variation	*T* equals total percentage scores													
				KW		NY		P		SH		SC		W		General average	
				T	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.
		in.	*Direct Cr.*	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Z 16	XXI alloy	0	Cold 0.0001	13	−1	8	+3	16	−3	8	0	43	•+17	36	•+20	21	+6
Z 31	XXIII alloy	0	Hot 0.0001	14	0	4	−1	20	+1	8	0	6	•−20	4	•−12	9	−6
Z 33	do	0	Cold 0.0001	14	0	4	−1	20	+1	9	+1	30	+4	8	−8	14	−1
			Average	14	0	5	±2	19	±2	8	0	26	±14	16	±13	15	±4
Z 48 ▸	XXIII alloy	0.00020	HS	26		5		12		3		26		16		15	
Z 2	Rolled zinc	.00030	do	57	+10	21	+7	27	+3	24	+8	83	•+27	64	•+21	46	•+13
Z 24	XXIII	.00030	do	37	−10	7	−7	20	−4	7	−9	29	•−27	22	•−21	20	•−13
			Average	47	±10	14	±7	24	±4	16	±9	56	±27	43	±21	33	±13
Z 1	Rolled zinc	0.00050	HS	53	−9	31	•+11	32	+9	41	•+17	91	0	73	+4	54	+6
Z 5	do	.00050	Duplex HS, S	67	+5	24	+4	16	−7	32	+8	93	+2	78	+9	52	+4
Z 11	XXI	.00050	HS	66	+4	27	+7	33	+10	29	+5	91	0	84	•+15	55	+7
Z 12	do	.00050	Duplex HS, S	57	−5	12	−8	16	−7	11	•−13	97	+6	76	+7	45	−3
Z 22	XXIII	.00050	HS	61	−1	14	−6	20	−3	16	−8	87	−4	55	•−14	42	−6
Z 35	do	.00050	Duplex HS, S	69	+7	12	−8	20	−3	13	•−11	87	−4	47	•−22	41	−7
			Average	62	±5	20	±7	23	±7	24	±10	91	±3	69	±12	48	±6
Z 6	Rolled zinc	0.00050	Cu, Ni(S)	62	•+19	19	+6	24	+7	20	+5	72	−8	63	•+13	43	+7
Z 14	XXI	.00050	do	41	−2	11	−2	16	−1	14	−1	83	+3	56	+6	37	+1
Z 40	XXIII	.00050	do	34	−9	11	−2	16	−1	13	−2	83	+3	40	−10	33	−3
Z 43	do	.00050	do	35	−8	9	−4	12	−5	11	−4	80	0	39	•−11	31	−5
			Average	43	±10	13	±4	17	±4	15	±3	80	±4	50	±10	36	±4

• Sets differing by more than 10 percent from average of comparable sets.
▸ Not included in average.

TABLE 20.—*Effect of variations in thickness of nickel (plus copper) on zinc and zinc die castings*—Continued

[HS, high sulfate nickel bath; S, standard nickel bath. Scores for all defects. Unless otherwise noted, Cr=0.00002 in. Tests started in 1936; total time 2.2 years]

Set	Basis metal	Thickness Ni (+Cu)	Variation	*T* equals total percentage scores													
				KW		NY		P		SH		SC		W		General average	
				T	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.	*T*	Dev. from avg.
				%	%	%	%	%	%	%	%	%	%	%	%	%	%
Z 13	XXI	0.00100	Duplex HS, S	64	−4	30	+4	24	−9	47	+4	90	−1	87	+3	57	0
Z 17	do	.00100	HS	76	+8	32	+6	43	+10	48	+5	95	+4	94	+10	65	+8
Z 37	XXIII	.00100	Duplex HS, S	65	−3	22	−4	32	−1	40	−3	92	+1	80	−4	55	−2
Z 47	do	.00100	HS	66	−2	19	−7	32	−1	36	−7	86	−5	74	−10	52	−5
			Average	68	±4	26	±5	33	±5	43	±5	91	±3	84	±7	57	±4
Z 15	XXI	0.00100	Cu, Ni(S)	62	−4	28	+3	44	[a]+14	45	+4	88	0	87	+1	59	+3
Z 41	XXIII	.00100	do	67	+1	23	−2	20	−10	28	[a]−13	92	+4	86	0	53	−3
Z 45	do	.00100	Ni(HS), Cu, Ni(S)	69	+3	24	−1	27	−3	50	+9	84	−4	86	0	57	+1
			Average	66	±3	25	±2	30	±9	41	±9	88	±3	86	0	56	±2
Z 49	XXIII	0.00125	Cu, Ni(S)	71	-------	28	-------	36	-------	43	-------	95	-------	87	-------	60	-------
Z 38	do	.00200	Duplex HS, S	73	-------	30	-------	40	-------	60	-------	88	-------	82	-------	62	-------
Z 42	do	.00200	Cu, Ni(S)	65	-------	29	-------	59	-------	66	-------	84	-------	91	-------	66	-------

[a] Sets differing by more than 10 percent from average of comparable sets.

TABLE 21.—*Effect of variations in thickness of nickel (plus copper) on zinc and zinc die castings*

TABLE 21.—*Effect of variations in thickness of nickel (plus copper) on zinc and zinc die castings*

[HS, high sulfate nickel bath; S, standard nickel bath. Scores for all defects. Cr=0.00002 in. Tests started in 1938; total time 1.3 years]

Set	Basis metal	Thickness Ni (+Cu)	Variation	*T* equals total percentage scores													
				KW		NY		P		SH		SC		W		General average	
				T	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg
		in.		%	%	%	%	%	%	%	%	%	%	%	%	%	%
Z 48A*	XXIII	0.00020	HS	37		8		13		13		67		21		27	
Z 24A*	do	.00030	HS	36		8		13		10		66		27		27	
Z 22A	do	.00050	do	45		16		21		17		94		63		43	
Z 35A	do	.00050	Duplex HS, S	59		12		17		17		86		60		42	
			Average	52		14		19		17		90		62		42	
Z 40A*	do	.00050	Cu, Ni, (S)	50		16		19		16		88		70		43	
Z 51A	do	.00075	HS	63	−3	21	−1	33	+4	25	−2	98	0	76	−4	53	−1
Z 52A	do	.00075	Duplex Ni, HS, S	75	+9	23	+1	30	+1	34	+7	100	+2	82	+2	57	+3
Z 53A	do	.00075	Cu, Ni (S)	61	−5	23	+1	28	−1	28	+1	93	−5	79	−1	52	−2
Z 61A	XXI	.00075	do	65	−1	22	0	25	−4	22	−5	99	+1	81	+1	52	−2
			Average	66	±5	22	±1	29	±3	27	±4	98	±2	80	±2	54	±2
Z 37A	XXIII	.00100	Duplex HS, S	79		31		31		63		98		94		66	
Z 41A	do	.00100	Cu, Ni (S)	66		30		22		36		94		95		57	
Z 38A	do	.00200	Duplex HS, S	85		53		58		69		98		99		77	
Z 42 A	do	.00200	Cu, Ni (S)	76		54		58		70		96		99		74	

* Not included in average.

TABLE 22.—*Effect of variations in thickness of chromium over nickel (plus copper) on zinc die castings*

[Tests started in 1936; total time 2.2 years. Total thickness=0.0005 in.]

Set	Basis metal	Coating		*T* equals total percentage scores													
				KW		NY		P		SH		SC		W		General average	
		Composition	Cr thickness	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg
			In.	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Z 19	XXIII	Ni, Cr	0	22	*−31	6	−7	12	−9	9	−8	39	*−42	28	*−31	19	*−22
Z 4	Rolled Zn	do	0.00001	65	*+12	13	0	16	−5	16	−1	97	*+16	76	*+17	47	+6
Z 25	XXIII	do	.00001	59	+6	9	−4	20	−1	13	−4	92	+11	55	−4	41	0
Z 36	do	Cu, Ni, Cr	.00001	51	−2	13	0	20	−1	11	−6	79	−2	55	−4	38	−3
Misc	(Table 20)	Ni, Cr	.00002	62	+9	20	+7	23	+2	24	+7	91	+10	69	+10	48	+7
Z 3	Rolled Zn	do	.00003	57	+4	20	+7	32	*+11	34	*+17	89	+8	77	*+18	52	*+11
Z 26	XXIII	do	.00003	55	+2	10	−3	23	+2	12	−5	83	+2	53	−6	39	−2
		Average		53	±8	13	±4	21	±4	17	±7	81	±13	59	±13	41	±7

* Sets differing by more than 10 percent from average of comparable sets.

TABLE 23.—*Effect of variations in thickness of chromium over nickel (plus copper) on zinc die castings*

[Tests started in 1938; total time 1.3 years. Total thickness=0.00075 in.]

Set	Basis metal	Coating		*T* equals total percentage scores													
				KW		NY		P		SH		SC		W		General average	
		Composition	Cr thickness	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg
			In.	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Z 54A	XXIII	Cu, Ni, Cr	0.00001	54	*−15	18	−3	20	−8	28	−8	100	+3	81	−3	50	−6
Z 53A	do	do	.00002	61	−8	23	+2	28	0	28	−8	93	−4	79	−5	52	−4
Z 55A	do	do	.00003	80	*+11	23	+2	35	+7	40	+4	99	+2	92	+8	62	+6
Z 56A	do	do	.00005	79	+10	18	−3	27	−1	47	*+11	94	−3	85	+1	58	+2
		Average		69	±8	21	±3	28	±4	36	±8	97	±3	84	±4	56	±5

* Sets differing by more than 10 percent from average of comparable sets.

TABLE 24.—*Effect of "bright nickel" on zinc die castings*

• Sets differing by more than 10 percent from average of comparable sets.

TABLE 24.—*Effect of "bright nickel" on zinc die castings*

[Tests started in 1938; total time, 1.3 years. All coatings 0.00025 in. Cu; 0.0005 in. Ni; 0.00002 in. Cr]

Set	Basis metal	Type of nickel	*T* equals total percentage scores													
			KW		NY		P		SH		SC		W		General average	
			T	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg	*T*	Dev. from avg
			%	%	%	%	%	%	%	%	%	%	%	%	%	%
Z 53A	XXIII	Plain	61	−1	23	−3	28	−2	28	−3	93	−2	79	+2	52	−3
Z 53B	do	Bright, not buffed	70	+8	39	•+13	35	+5	50	•+19	94	−1	78	+1	61	+6
Z 53B	do	Bright, buffed	66	+4	21	−5	23	−7	25	−6	96	+1	82	+5	52	−3
Z 53E, G, H	do	Bright, commercial plants	51	•−11	20	−6	22	−8	27	−4	92	−3	73	−4	48	−7
Z 61A	XXI	Plain	65	+3	22	−4	25	−5	22	−9	99	+4	81	+4	52	−3
Z 61B	do	Bright, not buffed	71	+9	32	+6	43	•+13	38	+7	98	+3	78	+1	60	+5
Z 61B	do	Bright, buffed	65	+3	27	+1	42	•+12	26	−5	96	+1	76	−1	55	0
Z 61E, G, H	do	Bright, commercial plants	50	•−12	24	−2	24	−6	30	−1	90	−5	71	−6	48	−7
		Average	62	±6	26	±5	30	±7	31	±7	95	±3	77	±3	55	±4

• Sets differing by more than 10 percent from average of comparable sets.

(2) *Effect of method of nickel plating;* (a) *High-sulfate and duplex coatings.*—It is not possible to deposit satisfactory coatings of nickel directly on zinc from ordinary nickel baths, such as the "standard." Adherent nickel may be deposited from the "high-sulfate" bath and, if desired, an additional thickness may then be applied from the standard bath to form a "duplex" nickel coating. Comparison of deposits produced entirely from the high-sulfate bath with the duplex nickel deposits shows no significant differences. However, the high-sulfate deposits are usually more brittle than the standard nickel. Especially if they are as thick as 0.001 in., coatings from the high-sulfate bath deposited on irregularly shaped articles are more likely to crack in service than the duplex coatings.

(b) *Bright nickel.*—The average proprietary bright nickel deposits (table 24) including those produced in the three commercial plants, were at least as protective as the plain nickel, though there was more cracking of the bright coatings.

(3) *Effect of a copper layer.*—Instead of using an initial layer of high-sulfate nickel on the zinc, most commercial plants now apply an initial layer of copper from some type of cyanide bath, such as the rochelle-salt bath, and follow this with regular nickel or bright nickel. The data in table 20 show that with coatings having a total thickness of 0.0005 in. the copper layer furnished no added protection, that is, the score was about the same as that with only the thickness of nickel that was present (in this case 0.0003 in.). With a total thickness of 0.001 in. or more, the scores were about the same with and without copper; in other words, the copper layer furnished about as much protection as an equal thickness of nickel. It is necessary to have an appreciable thickness of nickel, at least 0.0003 in., over the copper to prevent surface copper stains on exposure. The rating for set Z 50 (not in table 20), which had a layer of copper but no nickel under the chromium, was low in all locations (as might be expected from the behavior of chromium plated directly on sheet copper, table 14).

(4) *Effect of thickness of chromium.*—The data in table 22 show little difference in scores for 0.00001 to 0.00003 in. of chromium over 0.0005 in. of nickel on zinc. Table 23 shows that 0.00005 in. of chromium over 0.00075 in. of copper plus nickel on zinc has no such detrimental effect as was observed with this thickness of chromium over nickel on brass. The absence of severe cracking through to the zinc may be caused by the greater total thickness of coating and also by the greater ductility of the copper layer.

(5) *Effect of the basis metal.*—Table 20 shows that for comparable coatings the rolled zinc was slightly, but consistently, better than the die-castings. There was no appreciable difference in the behavior of the two types of die-castings.

V. COMPARISON OF DIFFERENT BASIS METALS

For certain purposes the choice of both the basis metal and the coating may depend upon the thickness of the coating required to furnish satisfactory protection on the metal selected. The average scores for 1 year's exposure in six locations with nickel and chromium coatings on the three types of basis metal are plotted in figure 4. If

a score of 60 percent, that is an average rating of 3 for the year, is used as the basis of comparison, this degree of protection requires on brass about 0.0002 in. of nickel, on zinc and die-castings about 0.0007 in., and on steel about 0.00085 in. These thicknesses are purely relative, but their order would not be changed if another criterion, such as a score of 70 percent, were employed. These values indicate the relative magnitudes that might be employed in specifications for coatings on the three types of basis metal for about the same service.

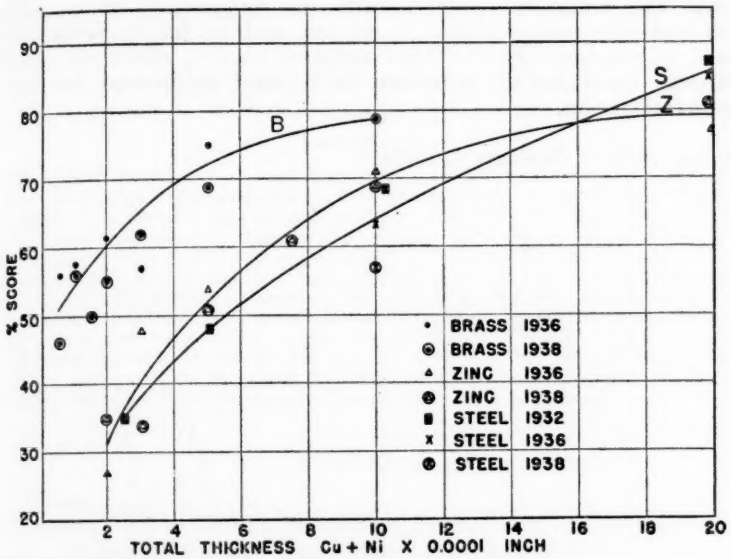

FIGURE 4.—*Effect of thickness of nickel (or of nickel plus copper) on percentage scores for 1 year of exposure.*

Average of 6 locations. All final nickel coatings covered with 0.00002 in. of chromium.

VI. CONCLUSIONS

1. The most important factor in the protective value of nickel-chromium coatings on steel, brass, or zinc is the thickness of the nickel coatings.

2. On steel or zinc, a layer of copper under the nickel adds little to the protective value of thin coatings. With thick deposits, the protective value of the composite coating approaches, but does not exceed, that of a nickel coating of the same total thickness.

3. Variations in the methods of preparation and of nickel plating, which included the use of four bright nickel solutions supplied in 1938, had no large effects upon the protective value of the coatings.

4. Variations in the thickness of the chromium coating from 0.00001 to 0.00003 in. applied over nickel have very little effect, but if it is 0.00005 in. or more, cracking is likely to occur, especially over nickel coatings on brass.

5. Variations between basis metals of a given group have no large effects. A greater thickness of nickel is required to furnish a given degree of protection on zinc than on brass, and greater on steel than on zinc.

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THERMODYNAMIC PROPERTIES OF SULFURIC-ACID SOLUTIONS AND THEIR RELATION TO THE ELECTROMOTIVE FORCE AND HEAT OF REACTION OF THE LEAD STORAGE BATTERY

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ABSTRACT

The heat of reaction in a lead storage cell involves reactions at the positive and negative plates and changes in the heat content of sulfuric-acid solutions. The latter is a variable factor, depending on the concentration of the solution. Newly computed values of the partial molal heat contents have made possible more accurate values of the heat of reaction, based on thermochemical data for comparison with similar values computed from the best available electrochemical data. Good agreement was found. The partial molal heat capacity of sulfuric-acid solutions has also been recalculated. Critically selected values of electromotive force and temperature coefficient are given. These include previously unpublished values obtained at this Bureau in 1933. The partial molal volumes of sulfuric-acid solutions are given for a few concentrations and these are used for computing changes in electromotive force with change in pressure.

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I. INTRODUCTION

In a previous paper by the authors [1],[1] it was shown that the double-sulfate theory of reactions in the lead storage battery expressed by the equation

$$PbO_2+2H_2SO_4+Pb\rightleftharpoons 2PbSO_4+2H_2O$$

is consistent with the observed amounts of acid consumed and water formed when the cell is discharged. The experiments described in

[1] Figures in brackets indicate the literature references at the end of this paper.

that paper involve no assumptions regarding the correctness or applicability of any theory of the chemical reaction. The facts, established by experimental work, are (1) that 2.02 ± 0.03 equivalents of acid are used, and (2) that 1.96 ± 0.19 equivalents of water are formed by the passage of 1 faraday of electricity through the cell in the discharge direction. Thus to a higher degree of accuracy than previously attained, the results confirm the double-sulfate theory of chemical reactions in the battery.

Having established the reaction, thermodynamic reasoning may be used in comparing the heat of the reaction based on thermochemical data with calculations based on electrochemical data. Dolezalek [2] and others have made such comparisons previously on the assumption that the double-sulfate theory is correct, but more reliable thermal and electrical data are now available.

The data given in this paper on the properties of sulfuric acid have much wider application, however, than to the specific problem which is discussed.

II. THERMOCHEMICAL DATA FOR SULFURIC ACID

1. RELATIVE HEAT CONTENT OF SOLUTIONS

The energy changes (heat of reaction) in a storage cell involve all the constituents, including plates, and changes in the heat content of the solutions. For the solids, definite values of the heat of formation are available, and these values do not vary with the concentration of the solution. The variable factor depends on the concentration of the solutions, and the calculation of the heat of reaction involves the partial molal quantities for the solutions. These are, according to the nomenclature of Lewis and Randall [3],

$\overline{H}_1$=partial molal heat content of the water, and
$\overline{H}_2$=partial molal heat content of the acid.

The heat content of a particular solution is given by the equation

$$H=n_1\overline{H}_1+n_2\overline{H}_2, \tag{1}$$

where n_1 and n_2 are the number of moles of water and acid, respectively. If we deal with 1 mole of solution, this equation may be expressed in terms of mole fractions, N_1 and N_2 of the constituents.

Since

$$N_1=\frac{n_1}{n_1+n_2} \text{ and } N_2=\frac{n_2}{n_1+n_2} \text{ and } N_1+N_2=1,$$

eq 1 becomes, for 1 mole of solution,

$$H=N_1\overline{H}_1+N_2\overline{H}_2. \tag{2}$$

Practically, the experimental data from which the partial quantities are calculated are based on observations of the heat liberated as increasing quantities of water are added to a specified amount of H_2SO_4, for example, 1 mole of H_2SO_4. These data are given in a table published by Bichowsky and Rossini [4]. However, these data are for a temperature of 18° C and require correction factors

to convert them to 25° C, if the results of the thermochemical calculations are to be compared with observed electrochemical data on batteries at 25° C. Dr. Rossini has kindly supplied the corrections to convert his published data to 25° C. Furthermore, this is the temperature at which measurements in dilute solutions have been made recently by Lange, Monheim, and Robinson [5].

Following the nomenclature in a paper by Rossini [6], Heat Contents in Aqueous Solutions, the relative apparent molal heat content of the solute is designated as $\Phi_h - \Phi_h'$, where Φ_h' is the apparent molal heat content at an arbitrarily chosen concentration. Taking the concentration $H_2SO_4.400H_2O$ as the starting point, values of $\Phi_h - \Phi_h'$ at 25° C were calculated and are given in column 4 of table 1. Those based on Rossini's data cover the range $n_1 = 6{,}400$ to $n_1 = 0$.

TABLE 1.—*Heat content of sulfuric-acid solutions*

Concentration of solutions			Relative apparent molal heat content of H_2SO_4 at 25° C		$\frac{d(\Phi_h - \Phi_h^\circ)}{d\,(m^{1/2})}$	Relative partial molal heat content of—	
n_1, moles of water per mole of H_2SO_4	Molality of H_2SO_4	H_2SO_4	$\Phi_h - \Phi_h'$	$\Phi_h - \Phi_h^\circ$		H_2SO_4; $\overline{H}_2 - \overline{H}_2^\circ$	H_2O; $\overline{H}_1 - \overline{H}_1^\circ$
1	2	3	4	5	6	7	8
	m	%	*kcal/mole*	*kcal/mole*		*kcal/mole*	*kcal/mole*
∞	0	0	−5.02	0.00	33.0	0.000	0.000
51,200	.00108	.011	−3.86	1.16	30.8	1.665	.000
25,600	.00217	.021	−3.48	1.54	29.8	2.234	.000
12,800	.00434	.043	−2.94	2.08	27.4	2.889	.000
6,400	.00867	.085	−2.12	2.90	17.74	3.725	−.000$_1$
3,200	.01734	.17	−1.54	3.48	12.74	4.318	−.000$_3$
1,600	.03469	.34	−0.98	4.04	8.28	4.811	−.000$_5$
800	.06938	.68	−.47	4.55	5.54	5.280	−.000$_9$
400	.1388	1.34	.00	5.02	3.32	5.638	−.001$_5$
200	.2775	2.65	+.39	5.41	1.64	5.842	−.002$_3$
100	.5551	5.16	.60	5.62	0.72	5.888	−.002$_7$
80	.6938	6.37	.65	5.67	.58	5.912	−.003$_0$
60	.9251	8.32	.72	5.74	.54	6.000	−.004$_3$
50	1.1101	9.82	.76	5.78	.54	6.065	−.005$_7$
40	1.3876	11.98	.84	5.86	.58	6.201	−.008$_8$
30	1.8502	15.36	.95	5.97	.70	6.446	−.015$_9$
25	2.2202	17.88	1.05	6.07	.82	6.681	−.024$_4$
20	2.7753	21.40	1.21	6.23	1.04	7.096	−.043$_3$
15	3.7004	26.63	1.53	6.55	1.40	7.896	−.089$_8$
12	4.626	31.20	1.89	6.91	1.79	8.834	−.160$_4$
10	5.551	35.25	2.28	7.30	1.98	9.632	−.233$_2$
8	6.938	40.49	2.86	7.88	2.20	10.777	−.362$_2$
6	9.251	47.57	3.78	8.80	2.25	12.222	−.570$_4$
5	11.101	52.13	4.43	9.45	2.30	13.282	−.766$_3$
4	13.876	57.65	5.39	10.41	2.24	14.581	−1.042$_9$
3	18.502	64.47	6.64	11.66	2.06	16.089	−1.476$_4$
2	27.75	73.13	8.56	13.58	1.76	18.216	−2.317$_8$
1.5	37.00	78.40	9.85	14.87	1.49	19.401	−3.021$_1$
1.0	55.51	84.48	11.70	16.72	1.27	21.451	−4.730$_9$
0.5	111.01	91.59	14.71	19.73	0.64	23.102	−6.742$_7$
		93.19		20.35			
0	∞	100.00	18.52	23.54	.00	23.54	

If Φ_h° represents the apparent molal heat content at infinite dilution, then

$$\Phi_h - \Phi_h^\circ = (\Phi_h - \Phi_h') + (\Phi_h' - \Phi_h^\circ).$$

The first term on the right-hand side of the equation being known, it is necessary to find the value of the second term in order to evaluate $\Phi_h - \Phi_h^\circ$ throughout the entire range of concentrations.

Plotting on separate sheets, tc the same scale, Rossini's data for $\Phi_h - \Phi_h'$ and the data of Lange, Monheim, and Robinson [5] for $\Phi_h - \Phi_h^\circ$ against the square root of the molality, for which the reason will appear later, one curve may be accurately fitted to the other in the range of overlapping values of Φ_h. Then the value, $\Phi_h' - \Phi_h^\circ$, is found to be 5.02 kcal/mole of H_2SO_4. Adding this to each value of $\Phi_h - \Phi_h'$ in column 4 of table 1, the values of $\Phi_h - \Phi_h^\circ$ given in column 5 are obtained. These values are the apparent molal heat contents of the respective solutions relative to infinite dilution. For concentrations below $n_1 = 6400$, the values of $\Phi_h - \Phi_h^\circ$ have been supplied from the data of Lange, Monheim, and Robinson.

When sulfuric acid is diluted with water, the amount of heat liberated in passing from any one state of dilution to any other state of greater dilution can be found at once by subtracting the value of $\Phi_h - \Phi_h^\circ$ for the greater dilution from the value of the same function at less dilution. A table of the heats of dilution can be readily calculated by subtracting the successive values of $\Phi_h - \Phi_h^\circ$ from the value for 100-percent acid, 23.54 kcal/mole of H_2SO_4. Concentrated acid available commercially, however, is normally 93.19 percent (66° Baumé), and if this is used, the heat liberated by diluting it is found by subtracting the respective values of $\Phi_h - \Phi_h^\circ$ from the value for 93.19 percent, which is shown by the table to be 20.35 kcal/mole of H_2SO_4.

2. RELATIVE PARTIAL MOLAL HEAT CONTENTS

If the heat of the storage-battery reaction is to be calculated from thermochemical data, it is necessary to know the heat changes that occur when H_2SO_4 is removed from and H_2O is added to an infinite amount of solution of some specified concentration, the process necessarily being isothermal. This involves the calculation of the relative partial molal values for H_2SO_4 and H_2O from the experimentally determined relative apparent molal values. The relation between these quantities is expressed by the equation

$$\Phi_h - \Phi_h^\circ = \overline{H}_2 - \overline{H}_2^\circ + \frac{n_1}{n_2}(\overline{H}_1 - \overline{H}_1^\circ),$$

in which $\Phi_h - \Phi_h^\circ$ is the relative apparent molal heat content, $\overline{H}_2 - \overline{H}_2^\circ$ and $\overline{H}_1 - \overline{H}_1^\circ$ are the relative partial molal heat contents of H_2SO_4 and H_2O, respectively.

Formulas for evaluating $\overline{H}_2 - \overline{H}_2^\circ$ and $\overline{H}_1 - \overline{H}_1^\circ$ are given in eqs 38 and 39 of Rossini's paper [6]. The molality being m, these equations are

$$\overline{H}_2 - \overline{H}_2^\circ = \Phi_h - \Phi_h^\circ + \frac{1}{2} m^{1/2} \frac{d}{dm^{1/2}}(\Phi_h - \Phi_h^\circ),$$

and

$$\overline{H}_1 - \overline{H}_1^\circ = -\frac{m^{3/2}}{2(55{,}508)} \frac{d}{dm^{1/2}}(\Phi_h - \Phi_h^\circ).$$

The values of $\Phi_h - \Phi_h^\circ$ being available, the tangents, $d(\Phi_h - \Phi_h^\circ)/d(m^{1/2})$, of the curve $\Phi_h - \Phi_h^\circ$ plotted against the square root of the molality can be evaluated. Values of the tangents at the respective points are given in table 1.

A prism of optical glass was used to obtain the tangents. A narrow band of paper having a small hole on the center line was fastened across the base of the prism vertically below the apex and parallel to it. A plotted point, when viewed from above, appeared as a double image through the hole in the paper. The prism was then rotated until the two arms of the curve, as viewed from above, were brought into coincidence at the apex of the prism. Either triangular face of the prism was then parallel to the tangent of the curve at the chosen point. To avoid systematic errors, readings were made by two observers with the prism in direct and reversed positions. Four or more determinations of the tangents were made at each plotted point, and these were all in satisfactory agreement. If the curvature was not too great, a prism having a base 4.8 by 3.5 cm was entirely satisfactory, but for a sharper curvature a smaller prism 2 by 2 cm was preferred.

In determining the tangents by this method, we are aware of the errors which may arise if the prism used is not of a suitable size for the particular curve. A too sharp curvature would prevent the use of such a method. This was not the case in this work. If one or at most a few tangents are to be measured, the method described would not be necessary, but in this work hundreds of tangents were measured and the use of the prisms made a great saving in time and increased the accuracy of the measurements. Another advantageous feature of the prisms was the ease and certainty with which the tangents could be measured at the required points.

As a further test of consistency of the measurements, the tangents were all plotted on a large scale against the square root of molality, and they were found to lie on a smooth curve. No adjustments were needed.

All the data necessary for calculating the partial molal quantities being available, the values of $\overline{H}_1-\overline{H}_1°$ and $\overline{H}_2-\overline{H}_2°$ at 25° C were tabulated in table 1. The heat capacity of the solutions will be treated similarly.

3. HEAT CAPACITY OF SOLUTIONS

Other equally important properties of sulfuric-acid solutions are the heat capacities and corresponding partial quantities which can now be calculated from measured values of specific heat. Having the data for both heat content and heat capacity, the thermodynamic properties of sulfuric-acid solutions can be calculated for a wide range of concentrations and temperatures.

The method of computing the partial molal heat capacities is essentially the same as for the heat contents [7]. The basis of the calculations is the experimental values of the specific heats reported by Biron [8]. In Biron's original paper, which was published in Russian, more determinations are given than those subsequently quoted in other publications. Socolik [9] quotes part of the earlier work of Biron at 20° and that of Savarizky at 40°, and adds his own work at 60° and 80° C. There is some uncertainty about the temperature applying to the values which he quotes from Biron. Actually, Biron's work was done at about 20° C, but the change in heat capacity with change in temperature is small, as shown by a comparison of Biron's values with those of Socolik and Savarizky. In the region of 30 to 40 percent solutions, the differences are very small.

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The results published by Bode [10], and Pascal and Garnier [11] have also been considered. These are in substantial agreement with Biron, but their determinations are far less numerous. The unpublished results of Taylor [12] for dilute solutions were of material help in drawing the curve of Biron's data. In addition to these authors there are many others whose results may be found in the technical literature. Biron's data, given in column 4 of table 2, cover the whole range of concentrations with numerous repeated observations at particular concentrations, and supply a consistent and comprehensive series of values. Smoothed values are given in column 5 of the same table. Although Biron's experiments are reported for 20° C, they apply satisfactorily to a temperature of 25° C. Comparing Biron's results at 20° with those of Savarizky at 40°, the greatest difference of 0.01 cal per gram degree occurs in the region 50- to 100-percent concentration. At concentrations of less than 40 percent, which includes the range for working batteries, the difference for a 20° interval does not exceed 0.005 cal per gram degree. The difference in specific heats for 20° and 25° C in this range is therefore about 0.001 cal per gram degree or less.

TABLE 2.—*Heat capacity of sulfuric-acid solutions*

Concentration of solutions			Specific heats, 20° C.		Apparent molal heat capacity, Φ_c	Tangents		Partial molal heat capacity of—	
n_1, moles of water per mole of H_2SO_4	Molality of H_2SO_4	H_2SO_4	Biron's average values	Smoothed values		$d\Phi_c/dm^{1/n}$	$d\Phi_c/dN_2$	H_2SO_4; $\overline{C}_{p_2}$	H_2O; $\overline{C}_{p_1}$
1	2	3	4	5	6	7	8	9	10
	m	%	*cal/g °C*	*cal/g °C*	*cal/mole °C*			*cal/mole °C*	*cal/mole °C*
1,600	0.0347	0.34	0.9968	0.9968	6.00	+11.40	----------	7.06	18.01
800	.0694	.68	.9937	.9937	6.85	+11.50	----------	8.37	18.01
400	.1388	1.34	.9877	.9877	8.10	+11.40	----------	10.22	18.01
200	.2775	2.65	.9764	.9762	9.82	+11.47	----------	12.84	18.00
150	.3700	3.50	.9688	.9688	10.80	+11.38	----------	14.26	17.99
100	.5551	5.16	.9551	.9549	12.32	+11.35	----------	16.55	17.97
50	1.110	9.82	.9171	.9177	15.85	+11.25	----------	21.78	17.90
30	1.850	15.36	.8768	.8767	19.35	+10.95	----------	26.80	17.77
20	2.775	21.40	.8339	.8339	21.94	+4.45	----------	25.64	17.53
19	2.921	22.27	.8277	.8275	22.10	+3.10	----------	24.75	17.88
18	3.084	23.22	.8203	.8205	22.27	+2.05	----------	24.07	17.92
17	3.265	24.25	.8122	.8127	22.32	+1.45	----------	23.63	17.94
16	3.469	25.39	.8041	.8041	22.39	+0.55	----------	22.91	17.98
15	3.700	26.63	.7948	.7945	22.40	−.40	----------	22.01	18.04
14	3.965	28.00	.7837	.7837	22.31	−1.15	----------	21.16	18.10
13	4.270	29.52	.7718	.7717	22.22	−2.05	----------	20.10	18.16
12.5	4.441	30.34	.7647	.7647	22.01	−2.43	----------	19.45	18.22
12	4.626	31.20	.7584	.7579	22.00	−2.85	----------	18.94	18.27
11	5.046	33.11	.7412	.7422	21.70	−3.90	----------	17.32	18.41
10	5.551	35.25	.7231	.7238	21.22	−4.70	----------	15.68	18.57
9	6.167	37.69	.7020	.7023	20.62	−5.02	----------	14.39	18.71
8	6.938	40.49	.6776	.6770	19.85	−5.12	----------	12.92	18.88
7	7.930	43.75	.6476	.6476	19.06	−3.15	----------	14.63	18.63
6	9.251	47.57	.6152	.6153	18.77	0.00	----------	18.77	18.02
5	11.101	52.13	.5805	.5801	19.06	+1.94	----------	22.29	17.37
4	13.876	57.65	.5420	.5420	20.15	+3.35	----------	26.39	16.46
3	18.502	64.47	.5012	.5012	22.20	+3.75	----------	30.26	15.33
2	27.753	73.13	.4628	.4628	26.03	----------	+49.6	37.05	12.31
1.5439	35.952	77.91	.4518	.4518	29.06	----------	+50.6	41.13	10.29
1.25	44.406	81.33	----------	.4481	31.52	----------	+41.0	41.64	9.02
1.1555	48.038	82.49	.4467	.4467	32.29	----------	+34.5	40.87	10.39
1.0	55.51	84.48	.4408	.4408	33.16	----------	+11.7	36.08	15.09
0.9246	60.03	85.48	.4346	.4346	33.20	----------	0.0	33.20	18.02
.6483	85.62	89.36	.4016	.4016	32.40	----------	−13.38	29.21	22.94
.4856	114.30	91.81	.3787	.3787	31.70	----------	−7.17	30.12	21.27
.2976	186.51	94.82	.3554	.3554	31.40	----------	+0.10	31.42	17.96
.1428	388.70	97.44	.3404	.3404	31.68	----------	+4.95	32.22	14.23
.000	∞	100	.3352	.3352	32.88	----------	+15.08	32.88	2.94

Having obtained smoothed values for Biron's published data, the apparent molal heat capacity, Φ_c, was calculated. Letting c_p represent the heat capacity of 1 g of solution (Biron's smoothed data), and c_p° the heat capacity of 1 g of water, which is unity by definition,

$$\Phi_c=\frac{1000}{m}(c_p-c_p^\circ)+98.076c_p.$$

Values of Φ_c are given in column 6 of table 2. These were plotted against the square root of molality and against the mole fractions for ranges of concentration indicated in table 2. The values of the tangents shown in columns 7 and 8 were obtained by methods previously described in this paper.

4. PARTIAL MOLAL HEAT CAPACITIES

Having the values of Φ_c and $d\Phi_c/d(m^{1/2})$, the partial molal heat capacities for H_2SO_4 and for water can be calculated by the following equations, respectively:

$$\overline{C}_{p_2}=\Phi_c+\tfrac{1}{2}\left(m^{1/2}\frac{d\Phi_c}{d(m^{1/2})}\right),$$

and

$$\overline{C}_{p_1}=\overline{C}_{p_1}^\circ-\frac{m^{3/2}}{111.016}\frac{d\Phi_c}{d(m^{1/2})},$$

where $\overline{C}_{p_1}^\circ$ is equal to the heat capacity of 1 mole of water. In the range of concentrated solutions, the corresponding equations used for calculating values of $\overline{C}_{p_2}$ and $\overline{C}_{p_1}$ are

$$\overline{C}_{p_2}=\Phi_c+N_1N_2\frac{d\Phi_c}{dN_2}$$

and

$$\overline{C}_{p_1}=\overline{C}_{p_1}^\circ-N_2^2\frac{d\Phi_c}{dN_2}.$$

In these equations the mole fractions of water and H_2SO_4 are indicated by N_1 and N_2, respectively. Values for $\overline{C}_{p_2}$ and $\overline{C}_{p_1}$ are given respectively in columns 9 and 10 of table 2.

One of the principal objects of the present work is to compare the results of thermal and electrical measurements by the application of thermodynamic theory. However, further calculations of the thermal properties of the materials involved are deferred until the electrical data have been presented and brought to the same point of being ready to calculate the heat of reaction electrochemically.

III. ELECTROCHEMICAL DATA OF STORAGE BATTERIES

1. ELECTROMOTIVE-FORCE DATA

Many determinations of the emf of the storage battery as a function of the acid concentration have been made. A summary of the values reported by nine observers appeared in the second but not in the third edition of a book by one of the present authors [13]. Considerable differences between the various determinations are apparent. These differences can be attributed in part to uncertainties in (1) the electrical units employed by the earlier observers, (2) the concentrations of solutions, particularly the conversion of degrees Baumé to specific gravities or densities, (3) the temperatures at which the observations were made, and (4) the condition of the plates, some having been removed from the cells and washed. It is perhaps surprising that the differences, as shown in the table, are not greater. Most of the earlier papers are lacking in details which now seem essential for evaluating the results.

After a critical examination of these earlier determinations, those of Dolezalek [2], Kendrick [14], Thibaut [15], and Vinal and Altrup [13] were selected for inclusion in table 3. Some of these measurements were made at 25° C, and for the others sufficient data were given for calculating the results to 25° C. The mean values for these four sets of data are given in column 7 of table 3.

TABLE 3.—*Electromotive force of lead-acid storage cells*

Specific gravity, $\frac{25°\ C}{25°\ C}$	H_2SO_4	Determinations on storage batteries, emf at 25° C						emf at 25° C; calculated from electrode measurements			
		Dolezalek 1898, calculated to 25° C	Kendrick 1900 at 25° C	Thibaut 1913, calculated to 25° C	Vinal and Altrup 1922, at 25° C	Mean of early values	NBS 1933, at 25° C	Vosburgh and Craig 1929	NBS 1933	Harned and Hamer 1935	Mean
1	2	3	4	5	6	7	8	9	10	11	12
	%	v [1]	v	v	v	v	v	v	v	v	v
1.020	3.05	-------	1.844	1.833	-------	1.839	1.855	1.856	-------	1.855	1.855
1.030	4.55	-------	1.871	1.851	-------	1.861	1.876	1.878	1.882	1.878	1.879
1.040	6.04	-------	1.889	1.867	1.890	1.882	1.892	1.893	1.896	1.895	1.895
1.050	7.44	1.906	1.902	1.879	1.903	1.898	1.905	1.909	1.908	1.908	1.908
1.100	14.72	1.963	1.954	1.941	1.956	1.953	1.962	1.962	1.961	1.960	1.961
1.150	21.38	2.012	2.000	1.944	2.000	1.989	2.005	2.006	2.007	2.005	2.006
1.200	27.68	2.054	2.044	2.043	2.045	2.047	2.050	2.049	2.051	2.049	2.050
1.250	33.80	2.098	2.084	2.094	2.091	2.092	2.098	-------	2.094	2.097	2.096
1.280	37.40	2.125	2.110	2.126	2.119	2.120	2.128	-------	2.121	2.127	2.124
1.300	39.70	2.143	2.127	2.148	2.138	2.139	2.148	-------	2.140	2.147	2.143

[1] International volts.

In column 8 of table 3 are given the results of a series of measurements made by the present authors in 1933 on pasted plates. Each cell contained two pasted plates which were made in the laboratory, using grids containing no antimony. The plates were therefore substantially free from local action, and ample time could be allowed for equilibrium to be established. Each cell contained a relatively large amount of electrolyte, the concentration of which was determined by weight titrations. Subsequently the plates were assembled in one

cell, which was used for studying the chemical reactions in the lead storage battery. The paper on this subject by the present authors [1] contains a further description of the preparation of these plates.

All of the emf measurements were made on a potentiometer, using a standard cell connected in opposition. The standard cell was compared at frequent intervals with the Bureau's primary standard for the volt. This arrangement had the advantage of bringing all the measurements within the range of the potentiometer without the necessity of using a volt box, and significant errors in the calibration of the potentiometer were avoided. Each entry in the table is the mean value of two series of measurements. The first series was completed several months before beginning the second series, but the results were concordant to within a few millivolts.

Comparing the NBS values of 1933 with the earlier values, it is seen that with few exceptions the NBS values are higher. Although the reasons for this are not certainly known, it is probable that the presence of antimony in the grids of plates used in the previous investigations resulted in some local action, the effect of which would be to decrease slightly the concentration of electrolyte in the pores of the plates. Such an effect, if present, must have been much less in the NBS experiments of 1933. Commercial plates with antimony grids are typical of the lead storage battery, but those without antimony most nearly represent the conditions for the fundamental equation of the battery, as expressed by the double-sulfate theory. It is evident from this table that the emf of the lead storage battery may be uncertain by several millivolts.

An independent method of obtaining the emf and temperature coefficients is by electrode combinations. Calculations based on such measurements have been made, and the emf data are reported in columns 9, 10, and 11 of table 3.

Vosburgh and Craig [16] reported values for cells containing mercurous sulfate and five different preparations of lead dioxide. Computed values of the emf of the storage battery based on their measurements are given in column 9 of table 3. The method for doing this will become apparent from a more detailed discussion of the NBS (1933) measurements on electrodes which were next in chronological order. These were made by the present authors on cells of the mercurous sulfate-lead dioxide type. The solutions in the various cells covered a range of 6 to 40 percent of H_2SO_4. The emf measurements were made with a potentiometer while the cells were in a thermostatically controlled oil bath regulated to 25° C $\pm$0.01° C.

In constructing the cells, use was made of glass blanks of H-form similar to those ordinarily employed in making Weston normal cells. Two samples of lead dioxide were used. One of these was prepared electrochemically and the other by oxidation of Na_2PbO_3 by bromine in an alkaline solution.

If the emf of these cells, reaction 1 in table 4, is combined with the known emf of reactions 2 and 3, the emf of the lead storage battery, reaction 4 can be computed by the method indicated in the table. The emf of reaction 2 was determined previously by Henderson and Stegeman [17] and that of reaction 3 by Gerke [18]. Their values are given in table 4, together with their respective values of dE/dT, which will be discussed in the following section.

Harned and Hamer [19] reported the emf of lead dioxide-hydrogen cells containing sulfuric-acid solutions up to 40-percent acid. By combining the emf of these cells with the emf of other cells mentioned by them, they calculated the emf of the lead-acid storage cell. From a plot of their data, we have read the values given in column 11 of table 3.

TABLE 4.—*Electromotive force and value of* $\Delta E/\Delta T$ *for cell reactions*

[Values of a and b are dependent on molality of H_2SO_4 solutions]

Reactions	Electromotive force at 25° C	$\Delta E/\Delta T$
	v[a]	v/°C
1. $PbO_2(c)+2H_2SO_4(m=x)\ (aq)+2Hg(l)\rightleftharpoons PbSO_4(c)+Hg_2SO_4(c)+2H_2O(l)$	a	b
2. $Pb(Hg)\ (sat.)+Hg_2SO_4(c)\rightleftharpoons PbSO_4(c)+2Hg(l)$	0.9646	0.00017
3. $Pb(c)\rightleftharpoons Pb(Hg)\ (sat.)$	.0057	[b].00002
4. $PbO_2(c)+2H_2SO_4(m=x)\ (aq)+Pb(c)\rightleftharpoons 2PbSO_4(c)+2H_2O(l)$	a+0.9703	b+0.00019

[a] International volts.
[b] This is a rounded figure. The author (Gerke) gave 0.000017.

2. TEMPERATURE COEFFICIENT OF ELECTROMOTIVE FORCE

In order to calculate the heat of the storage battery reaction from electrochemical data, it is necessary to know also the temperature coefficient of emf. Of the earlier experimenters mentioned in table 3, only Dolezalek [2] and Thibaut [15] measured the temperature coefficients. Their values are given in columns 3 and 4 of table 5. The NBS results are also reported in table 5. The values in column 6 are mean results of the two series of measurements on pasted plates having pure lead grids.

TABLE 5.—*Change in electromotive force of the lead storage battery with change in temperature*

Specific gravity, $\frac{25°\ C}{25°\ C}$	H_2SO_4	Determinations on storage batteries, $\Delta E/\Delta T$				Calculated from electrode measurements, $\Delta E/\Delta T$			
		Dolezalek 1898, 0° to 24° C	Thibaut 1913, 15° to 50° C	Mean of early values	NBS 1933, 0° to 40° C	Vosburgh and Craig 1929	NBS 1933	Harned and Hamer 1935	Mean
1	2	3	4	5	6	7	8	9	10
	%	$mv/°C$	$mv/°C$	$mv/°C$	$mv/°C$	$mv/°C$	$mv/°C$	$mv/°C$	$mv/°C$
1.020	3.05	----------	−0.06	−0.06	----------	−0.05	----------	−0.05	−0.05
1.030	4.55	----------	+.02	+.02	----------	+.02	+0.04	+.01	+.02
1.040	6.04	−0.04	+.08	+.02	+0.10	+.07	+.09	+.05	+.07
1.050	7.44	+.06	+.13	+.10	+.15	+.11	+.12	+.08	+.10
1.100	14.72	+.34	+.26	+.30	+.29	+.22	+.24	+.20	+.22
1.150	21.38	+.36	+.29	+.32	+.33	+.25	+.27	+.23	+.25
1.200	27.68	+.31	+.28	+.30	+.30	+.23	+.26	+.22	+.24
1.250	33.80	+.24	+.25	+.24	+.22	----------	+.23	+.21	+.22
1.280	37.40	+.19	+.22	+.20	+.19	----------	+.20	+.20	+.20
1.300	39.70	+.16	+.20	+.18	+.18	----------	+.18	+.19	+.18

By following a procedure similar to that described above for computing the emf from electrode combinations, the temperature coefficient may be calculated as indicated in the last column of table 4.

The values thus determined are given in column 8 of table 5. Columns 7 and 9 of this table give the values found by Vosburgh and Craig [16] and Harned and Hamer [19].

It is believed that tables 3 and 5 contain the best data available on emf and temperature coefficient, respectively, of the lead storage battery. The tables show the consistency of measurements made at different times and in different places. At most, the differences in corresponding values are a few millivolts. These data are of practical importance in the operation of batteries, and are used in this paper as a basis for calculating the heat of reaction. These calculations will be compared with the values calculated from thermochemical data.

IV. HEAT OF THE LEAD STORAGE-BATTERY REACTION

1. BASED ON ELECTROCHEMICAL DATA

The thermodynamic relation between the electrical measurements and the heat of reaction is expressed by the Gibbs-Helmholtz equation, which, for the present purpose, may be written as follows:

$$\Delta H = -\frac{2 \times 96{,}500}{4.1833}\left(E - T\frac{dE}{dT}\right),$$

where ΔH is the heat of reaction in calories, 96,500 the value of the Faraday constant in international coulombs per equivalent, 2 the number of equivalents involved in the reaction, and 4.1833 the conversion factor to reduce the electrical measurements in international volt-coulombs to calories. Following the custom in thermochemical investigations in this country, the calorie used here is an artificial calorie defined as equal to 4.1833 international joules. As T, the absolute temperature, is 298.16° K, the equation becomes

$$\Delta H = -46{,}136\left(E - 298.16\frac{dE}{dT}\right).$$

Using the values of E and dE/dT given in tables 3 and 5, the heat of reaction, ΔH, has been computed for the respective concentrations of sulfuric acid. The results of these calculations, based on electrochemical data, are given in columns 4, 5, and 6 of table 6. Column 4 of this table contains values of the heat of reaction based on the mean of determinations made on cells prior to 1933. These batteries were, it is believed, similar in materials and construction to batteries used commercially. In column 5, values for ΔH are given based on cell measurements made at this Bureau in 1933. They differed from the other cells of previous experiments in the fact that they contained no antimony. Column 6 contains values of ΔH computed from the mean of the electrode measurements. These electrodes are better adapted to precise measurements, because the purity of materials can be better assured, the temperature can more easily be controlled, and the electrodes are free from local action, which is more or less inevitable in a commercial type of storage cell.

TABLE 6.—*Heat of the lead storage-battery reaction*

[Comparison of the values calculated from thermal data with those calculated from electrical data.]

Specific gravity, $\frac{25°\ C}{25°\ C}$	H_2SO_4	Heat of reaction (thermochemical)	Heat of reaction (electrochemical)			Differences in heat of reaction. Electrochemical − thermochemical		
			Batteries; average value 1898 to 1922	Batteries; NBS values 1933	Electrodes; average value 1929 to 1935	Batteries, 1898 to 1922	Batteries, NBS 1933	Electrodes, 1929 to 1935
1	2	3	4	5	6	7	8	9
	%	*kcal*	*kcal*	*kcal*	*kcal*	%	%	%
1.018	[a]2.65	−86.29			−86.24			+0.05
1.020	3.05	−86.32	−85.68		−86.28	−0.75		+.05
1.030	4.55	−86.37	−85.50		−86.42	−.91		+.06
1.040	6.04	−86.43	−86.56	−85.92	−86.47	−.15	+.59	−.05
1.050	7.44	−86.53	−86.20	−85.83	−86.66	+.38	+.82	−.15
1.100	14.72	−87.44	−85.98	−86.54	−87.45	+1.70	+1.04	−.01
1.150	21.38	−88.87	−87.37	−87.97	−89.12	+1.72	+1.03	−.28
1.200	27.68	−90.99	−90.32	−90.46	−91.28	+0.74	+0.59	−.32
1.250	33.80	−93.65	−93.08	−93.77	−93.66	+.61	−.13	−.01
1.280	37.40	−95.37	−94.93	−95.57	−95.25	+.46	−.21	+.13
1.300	39.70	−96.51	−96.22	−96.63	−96.36	+.30	−.12	+.16
Average						±0.77	±0.57	±0.12

[a] This concentration corresponds to n_1=200 moles of H_2O.

The results for the electrode measurements are the mean of all the results reported in tables 3 and 5, beginning with those of Vosburgh and Craig in 1929 and including the later observations made at this Bureau in 1933 and the still later measurements of Harned and Hamer in 1935.

The NBS results of 1933 on batteries and electrodes have not been published previously, because at that time it was felt that more accurate determinations were needed to establish the chemical reactions occurring in the lead storage battery. The work of Vinal and Craig [1] published in 1935 strongly supports the double-sulfate theory, and affords the required foundation for comparing the heat of reaction of the battery calculated from electrochemical data with the heat of reaction calculated from purely thermal data.

2. BASED ON THERMOCHEMICAL DATA

In calculating the heat of reaction thermochemically, a dilute solution of sulfuric acid, having the proportions of 1 mole of acid to 200 moles of water was chosen as the starting point. The heat of formation, ΔHf, at 18° C, of the various constituents is written beneath their respective symbols.

$$PbO_2(c)+2[H_2SO_4+200H_2O](l)+Pb(c)\rightleftharpoons 2PbSO_4(c)+402H_2O(l)$$
$$-65{,}000 \qquad 2(-211{,}500) \qquad 0 \qquad 2(-218{,}500) \qquad 2(-68{,}370)$$

These values are taken from the book by Bichowsky and Rossini [4]. From these numerical values, the heat of reaction, ΔH, is −85,740 cal. A correction is necessary to convert this to the equivalent heat of reaction at 25° C, which is a more convenient temperature. Using a correction factor of 45.4 cal/° C for the reaction, as expressed by the

above equation, the heat of the reaction at 25° C becomes −85,420 cal. The minus sign indicates that the heat content of constituents on the right of the above equation is less than that of those on the left, and that heat is evolved in the reaction.

Considered from a purely chemical point of view, the changes in the heat content of sulfuric-acid solutions from one concentration to another vary by the amount of heat liberated as the solution is diluted. Eventually a point is reached when no more heat is liberated and the solution is infinitely dilute and its volume is infinitely great. The amount of heat energy liberated by the dilution process may be calculated from the relative apparent molal heat contents given in column 5 of table 1.

In order to calculate the heat of reaction for an infinitely dilute sulfuric-acid solution, this value must be added to this relative apparent molal heat content of a solution of $H_2SO_4 \cdot 200H_2O$. As shown by column 5 of table 1, this is 5.41 kcal (5410 cal) per mole. Two moles are involved, whence $-85{,}420+10{,}820=-74{,}600$ as the heat of reaction at infinite dilution. In a cell, however, the energy of the reaction depends on the differential changes in the heat contents, that is, upon the relative *partial* molal heats of the acid and the water. Values for these are given in columns 7 and 8 of table 1. At infinite dilution these values are zero and the heat of reaction in a cell is precisely the same as the thermochemical or calorimetric heat of reaction. At any finite concentration there is a difference, amounting to about 3 kcal/mole of H_2SO_4 for a solution containing 40 percent of H_2SO_4. With due regard for the algebraic signs, the heat of reaction as it occurs in a storage battery at any finite concentration equals the heat of reaction at infinite dilution plus twice the sum of the relative partial molal heat contents of H_2SO_4 and H_2O. The factor 2 comes from the use of 2 moles each of H_2SO_4 and H_2O for each mole of lead dioxide. These matters were more fully explained in an earlier part of this paper.

3. COMPARISON OF THERMOCHEMICAL AND ELECTROCHEMICAL DATA

Table 6 gives in parallel columns the heat of reaction calculated from thermochemical data and from electrochemical data throughout a range of acid concentrations from 2.65 to 39.70 percent. This covers the range used in lead-acid batteries.

The agreement is rather remarkable, considering the numerous sources of error. These include errors in determining the heat of formation of the various constituents and their heat capacities, and the errors of graphical methods of determining tangents for computing the partial quantities. On the electrochemical side, there are possible uncertainties and sources of error in measuring the emf and temperature coefficients as well as errors in temperature control.

The uncertainties about standards of emf and temperature control are probably greater in the earlier measurements on batteries, and this is perhaps the reason that these are not consistently in as good agreement with the later NBS measurements of 1933 or with the thermochemical calculations. One fact, however, seems clearly established, namely, that the fundamental chemical reaction, as expressed by the equation of the double-sulfate theory, must be correct. To have used

any other than 2 moles each of H_2SO_4 and H_2O for 2 faradays in the calculations would have resulted in large discrepancies. Good agreement between the heats of reaction based on thermochemical and electrochemical data may be regarded as a thermodynamic proof of the correctness of the double-sulfate theory.

The uncertainties in the heat of formation of the solids are probably greater than in the case of the solutions, but they are probably not more than one or at most a few percent of the heat of reaction of the cell. In comparing values for differing concentrations of acid, any error in the heat of formation of the solids becomes a constant factor, and the corresponding differences in electromotive force from one concentration to another should depend on the solutions alone. Shankman and Gordon [20] have recently determined the vapor pressure of aqueous solutions of sulfuric acid. Using their activities of water and their activity coefficients of H_2SO_4 for molal concentrations of one and six and interpolated values from column 10, table 3 of this paper, for corresponding concentrations, the differences in emf were found to be:

Shankman and Gordon (calculated from vapor pressure)----------Δemf--0.201 volt.
NBS electrodes of 1933 (observed)----Δemf--0.200 volt.

The agreement between our observed values and those calculated from their vapor-pressure measurements is very good over a wide range of acid concentrations.

Of the electrochemical measurements, the greatest uncertainty is in the measurement of the temperature coefficient, but this is not the predominating term of the electrochemical calculations. Probably the most accurately determined values of emf and its temperature coefficient are those derived from the electrode measurements, and it is significant that these are in the best agreement among themselves and with the thermochemical data. Column 9 in table 6 shows throughout an acid range from 3 to 40 percent of H_2SO_4 that the average difference of 11 comparisons of the heat of reaction is only ± 0.12 percent, with a maximum difference of 0.3 percent. Whatever uncertainty may attach to the heat of formation of the solids, the values which have been used must be very close to the true values; otherwise such close agreement of calculations based on entirely unrelated data would not be expected.

V. EFFECT OF PRESSURE ON ELECTROMOTIVE FORCE

Partial molal volumes of sulfuric acid and water may be calculated by following in a general way the procedure for obtaining analogous quantities of heat content and heat capacity. A few of the partial molal volumes have been calculated in order to estimate the change in emf with change in pressure. Inquiries about the magnitude of this effect are often made. Several attempts to measure the change experimentally have been reported. Gilbault [21], using 8.8 percent acid, found -0.0012 v per 100 atm, and Dolezalek [2], using 20 percent acid, found -0.0011 v per 100 atm increase in pressure. The minus sign is used to indicate a decrease in emf with increase in pressure. The agreement between these results is perhaps accidental.

The change in volume of the cell as a whole depends on the change in volume of each constituent. Actually, when a cell containing a solution of less than 37 percent of H_2SO_4 discharges, there is a small increase in volume. This should not be confused with the decrease in volume of the solution which occurs during the same process. Considering the equation for the reaction according to the double-sulfate theory, it is possible to write the molal volumes of the solid constituents and the partial molal volumes of the acid and water, and take the difference of the sums on the two sides of the equation. For example, a cell containing a 10-percent solution would give

Left side		Right side	
	ml		*ml*
PbO_2 (c)	25. 52	$2PbSO_4$ (c)	97. 83
Pb (c)	18. 27	$2H_2O(2\overline{V}_1)$ (aq)	36. 02
$2H_2SO_4(2\overline{V}_2)$ (aq)	78. 98		
Total	122. 77	Total	133. 85
		$\Delta V = 11.08$	

The difference is an increase of 11.08 ml in volume for the passage of 2 faradays in a discharge direction. The work done against an external pressure of 1 atm is 11.08 ml-atm. Since 1 liter-atm equals 101.33 v-coulombs, this difference produces a change of emf equal to −0.006 mv/atm. The change is very small and unimportant from an engineering point of view.

Calculated values for several concentrations within the range used in batteries are shown in table 7. Below 37 percent the values are negative, that is, the emf decreases with increased pressure. At about 37 percent the value of dE/dP is zero, and for higher concentrations the effect is positive.

TABLE 7.—*Change in electromotive force of a lead-acid storage cell with change in pressure*

[ΔV is the total change in volume of the cell, including the solid constituents and the solution at 1 atm]

Concentration of H_2SO_4		Density, $\frac{25°\ C}{4°\ C}$	Specific volume	Molal volume	Partial molal volumes		ΔV per 2 faradays	Equivalent volt-coulombs	dE/dP
Percent	Molality				Water, $\overline{V}_1$	Acid, $\overline{V}_2$			
1	2	3	4	5	6	7	8	9	10
			ml	*ml*	*ml*	*ml*	*ml*		*mv/atm*
5	0. 5262	1. 02996	0. 970911	18. 236	18. 03	39. 44	+11. 22	1. 137	−0. 0059
10	1. 1329	1. 06397	. 939876	18. 438	18. 01	39. 49	11. 08	1. 123	−. 0058
15	1. 7993	1. 09943	. 909562	18. 673					
20	2. 5490	1. 13649	. 879902	18. 945	17. 94	40. 85	8. 22	0. 833	−. 0043
25	3. 3987	1. 17504	. 851035	19. 263					
30	4. 3698	1. 21501	. 823038	19. 637	17. 76	43. 45	2. 66	. 270	−. 0014
35	5. 4903	1. 25628	. 796001	20. 077					
40	6. 7974	1. 29904	. 769799	20. 592	17. 57	45. 29	−1. 40	. 142	+. 0007
45	8. 3423	1. 34379	. 744164	21. 191					
50	10. 1962	1. 39113	. 718840	21. 882	17. 47	45. 90	−2. 82	. 286	+. 0015

VI. CONCLUSION

The authors' justification for assuming the double-sulfate theory of reactions rests on their previously published paper on the fundamental chemical reaction in the lead storage battery. This reaction having been verified by experimental results, the next step was to calculate the heat of reaction by thermodynamics. Before doing so, it was necessary to obtain better thermochemical data for sulfuric-acid solutions. The thermochemical tables presented in this paper have been compiled on the basis of critically selected data with the help of Dr. Rossini, to whom the authors make grateful acknowledgments. Similarly, a critical selection of emf and temperature coefficient data have been made, including some of the authors' experimental results. These data should be of engineering value in battery operation. It is of some interest that the average emf of a cell containing electrolyte of specific gravity 1.280 at 25° C, which is used in engineering work, is 2.125 v per cell. This ist he average resulting from long experience and measurements on many batteries. On the other hand, the laboratory measurements made with potentiometers and other precision equipment indicate 2.125 as the weighted mean value from electrode measurements and the NBS battery determination of 1933. Equally precise values are now available for other concentrations of electrolyte.

The Gibbs-Helmholtz equation was used to compute the heat of reaction from the electrochemical data. Comparing these results with the thermochemical calculations, it is seen that the agreement is remarkably good. To have assumed any other factor than 2 for the equivalents of H_2SO_4 and H_2O for the passage of 1 faraday would have resulted in large discrepancies. This fact may be regarded, therefore, as a thermodynamic proof of the validity of the double-sulfate theory of the chemical reaction.

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